A STUDY OF THE PITTING BEHAVIOR OF 316L AS-WELDED STAINLESS STEEL JOINTS IN $FeCl_3$ SOLUTION

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Abstract

316L stainless steels are widely used through out industry in potable water systems for their corrosion resistance. Welding of this material introduces a number of variables that can reduce the corrosion resistance and make the material subject to pitting corrosion. One such variable is the heat tint oxide that is produced during the welding process. This chromium rich layer is considered to be incoherent exposing the chromium depleted, and hence less resistant material to potentially corrosive environment. Literature suggests the pitting resistance of tinted material decreases with an increase in heat tint oxidation. The aim of this study was to test this correlation by producing welded samples with different degrees of heat tint and subject them to ASTM G48 Method A for pitting and crevice corrosion resistance. While the expected trend was not observed within the time frame of the experiments, important inferences on the pitting behavior of heat tinted stainless steel were made.

Key words: corrosion, pitting, 316L, stainless steel, heat tint, oxide, welding

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Abbreviations

AISI	American Iron and Steel Institute
ANSI	American National Standards Institute
ASM	American Society of Metals
ASTM	American Society for Testing Materials
AWS	American Welding Society
BCC	Body Centered Cubic
CFH	Cubic Feet per Hour
CPT	Critical Pitting Temperature
Cr	Periodic symbol for Chromium
E_{pit}	The electrochemical potential at which pitting initiates
GTAW	Gas Tungsten Arc Welding
GMA	Gas Metal Arc
HAZ	Heat Affected Zone
ISO	International Standards Organization
ISIJ	Iron and Steel Institute Journal
MIC	Microbiologically Induced Corrosion
NACE	National Association of Corrosion Engineers
NiDi	Nickel Development Institute
ppm	Parts per million

PTFE	Polytetrafluoroethylene (Teflon)
SMA	Submerged Metal Arc
UDC	Under Deposit Corrosion
316L	An austenitic stainless steel with typical chemical composition (in wt%) <0.03 C, 2.0 Mn, 0.75 Si, 0.045 P, 0.03 S, 16.0 – 18.0 Cr, 2.0 – 3.0 Mo, 10.0 – 14.0 Ni, 0.10 N

1. Introduction

Stainless steels are widely used in food processing, pharmaceutical, chemical, process engineering and water treatment and handling applications. Two principal reasons to consider the use of stainless steel in these applications are its resistance to corrosion and outstanding ability to resist contamination of potable water with any metal species found in stainless steel [1]. The corrosion resistance of stainless steels is due to the formation of a thin passivating chromium oxide film on the metal surface. This film spontaneously forms on clean metal when exposed to dry air or submersed in an oxidizing agent such as nitric acid. When immersed in water containing oxygen, there is a dynamic equilibrium that occurs between the alternate breakdown and repair of the oxide film [2]. The chromium oxide is tough and durable but there can be defects in the thin layer. When the environment becomes aggressive enough, such as in the presence of chloride ions, it can take advantage of the weakness in the film, initiating pitting corrosion [3].

300 series stainless steels are the most commonly used in potable water systems given their resistance to corrosion. 316L is a low carbon stainless steel with additions of molybdenum that make it more resistant to general corrosion and pitting/crevice corrosion than the conventional chromium-nickel austenitic stainless steels. Under properly controlled conditions, 316L is sufficient to meet the corrosion resistance requirements of a potable water system. However, the resistance of the weld metal and the heat affected zone (HAZ) is of greater interest since, as demonstrated in literature [4,

5] and in the author's own experience as demonstrated in the case studies below, these areas are more susceptible to localized corrosion than the parent material.

Given the aggressive, insidious behavior of pitting corrosion, it is important for engineers, inspectors and fabricators to understand the factors that influence the corrosion mechanism. While a single pit may be small in affected area and corroded volume, it can render systems inoperable as a result of loss of containment or multiple pits can go undetected decreasing the mechanical strength of a part or pipe with catastrophic consequences. Several important factors influencing pitting corrosion are reviewed. It is the purpose here to focus on the effects of heat tint scale on the corrosion resistance of stainless steel welds as this issue is one of the most dynamic, in that it can vary widely even when good control is exercised. Piping systems such as those used for potable water systems are often field installed. Choices of metallurgy and associated controls can be undermined by the challenges of field installations where confined space or limited access can make welding condition conducive to the creation of heat tint scale or oxide.

2. Statement of Objectives

Stainless steel has a long list of applications in industry including substitution for conventional materials. The austenitic stainless steel, particularly 316, is often chosen for its pitting and crevice corrosion resistance. There are however, issues surrounding the reduction in corrosion resistance of welded joints. As described below, there are a number of factors that have a detrimental affect on the corrosion resistance of welded 316L stainless steel. While a review of these factors is included, to examine each of these factors and their interaction in detail is well beyond the limited scope of this work.

It is the purpose here to examine the effects of heat tint scale on the corrosion resistance of stainless steel welds as this issue is one of the most dynamic in that it can vary widely even when good control is exercised. In addition to creating direct susceptibility to corrosion, heat tint can increase susceptibility to other corrosion mechanisms as explained in section 5.7.

Acceptance of heat tint scale is dependant on the predictability of the corrosion behavior of the metal under specific service conditions. It is understood the greater the heat tint as indicated by increasingly darker colors, the greater the reduction in pitting resistance. Based on this, there should be a predictable qualitative pattern to the corrosion behavior of heat-tinted welds exposed to similar environments. Experiments were undertaken to examine the pitting behavior of heat-tinted, as-welded joints and to demonstrate the predictability of corrosion performance.

Heat tinting of the welds was produced by varying the flow rate of backing gas, 99% argon, used during the welding process. As-welded samples were used in these experiments to ensure the influence of any metallurgical differences between the parent material, HAZ and weld metal could be examined. Samples were subjected to the pitting corrosion resistance test ASTM G48 method A [30] and examined to determine and categorize the influence of heat tint oxide on the corrosion of welded 316L joints.

3. Pitting Corrosion

Pitting corrosion is a localized form of corrosion by which cavities or "pits" develop in the material. Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to detect, predict and design against. Corrosion products often cover the pits making them difficult to find. A small, narrow pit with minimal overall metal loss can lead to the failure of an entire engineering system [4].

Pitting corrosion has two phases, pit initiation and pit propagation. The conditions under which each phase occurs can differ. Metallurgical characteristics such as microstructure or alloying element can have different effects on each phase.

3.1. The Pitting Mechanism

Pitting is a mode of corrosion that is associated with an occluded cell in which there is a small metal/solution interface that is restricted from the bulk solution. Typically, in pitting corrosion, the ratio of the cathodic to anodic areas is quite large. As a result, the current density and hence, the corrosion rate within the pit is large.

Pitting corrosion results from the localized breakdown or penetration of the passive film at a small discrete area. The result is a sharp discontinuity that can penetrate into the metal. Pits can also form under inoffensive corrosion products, chemical or biological films or other inert material.

In the presence of aggressive ions such as chloride, the ions breakdown the protective layer of chromium oxide, Cr_2O_3, by a competitive absorption mechanism in which

chloride ions move into the metal oxide interface at the metal surface. This process continues until a critical potential, E_{pit}, is reached. This potential corresponds to the concentration of chloride required to displace the oxygen from the protective oxide layer [6, 7]. Jones [4] states that the actual mechanism for pit initiation at E_{pit} is not clearly understood, but offers an expanded explanation of the above concept based on experimental observation.

3.2. Local Environments within Pits

Once a pit has been initiated, local conditions are altered such that pit growth is promoted. The cathodic and anodic electrochemical reactions of corrosion are spatially separate during pitting. Within the pit, the local environment becomes depleted of the cathodic reactant. This causes the cathodic reaction to shift to the exposed surface of the material outside of the pit. The pit environment becomes enriched by the anodic production of positively charge ions of iron, chromium and nickel. These ions attract the negatively charged chloride ion in to the pit to maintain charge neutrality. An insoluble corrosion product of $Fe(OH)_3$ creates a cap separating the electrolyte of the pit from the bulk solution. This cap impedes the migration of Fe^{2+} out of the pit but is porous enough to permit the migration of Cl^- into the pit sustaining a high acid chloride concentration and lowers the pH of the pit electrolyte. The result is an autocatalytic growth of a pit [4].

The hydrolysis of the metallic ions by:

$$Fe^{2+} + 2H_2O + 2Cl^- \rightarrow Fe(OH)_2 + 2HCl,$$

reduces the local pH. The acid chloride accelerates anodic dissolution, which in turn increases the chloride concentration within the pit. Y.C. Lu et al. [8] using tungsten microelectrodes measured the pH within a growing pit. It was discovered that the pH at the bottom of the pit was close to zero and the chloride concentration reached a value of 6 molar although an estimated value, calculated based on the solubility, is about pH 1.6. This enhancement of pH is reportedly explained by a formation of hydrochloro-complex of cations caused by the dissolution of metal but there has been little direct observation of it [9].

4. Environmental Factors Influencing the Pitting of 316L Piping Systems

Factors that influence the pitting corrosion of stainless steel are those that promote the break down of the naturally occurring protective oxide of stainless steel. These factors are a function of the design and manufacturing processes and operating conditions. The following list is not exhaustive, but a representation of the most common issues. In addition to the number of factors influencing the pitting of 316L, the degree to which they influence and interact with each other further complicates the study and control of pitting corrosion.

4.1. Temperature

Susceptibility to pitting increases with an increase in temperature. Higher temperatures provide greater thermal energy making the corrosive environment more aggressive. Pitting resistance is often characterized by the minimum temperature required to initiate pitting. This temperature is known as the Critical Pitting Temperature [4]. For 316L, the CPT of the unwelded metal ranges from approximately 12°C to 15°C in $FeCl_3$ solution. This value decreases for welded metal and the amount by which it decreases is a function of the weld parameters [5]. At temperatures above 70°C, the pitting potential becomes independent of the temperature [10].

4.2. pH

316L stainless steel is often used in pharmaceutical and food processing industries for its resistance to acidic environments. Under properly designed conditions, the environment should be compatible to the material of construction. Under such conditions, the pH of the bulk fluid has little effect on the corrosion rate or pitting susceptibility of 316L stainless steel [5]. As described below however, the pH has an effect on the form of free chlorine, which is frequently used to sanitize potable water systems fabricated from 316L, which can influence pit initiation.

4.3. Flow Velocity

When considering flow velocity, it is well known [10] that stagnancy is the worst condition to have. In stagnant or low-flow conditions, water-borne particles or sediments can settle on the bottom of the pipes providing initiation sites for pitting and crevice corrosion. These conditions also promote the attachment and buildup of biomaterial and bacteria on metal surfaces. A flow velocity of 1 m/s should prevent settling of particles and the buildup of organic material [11].

4.4. Dissolved Oxygen Concentration

Oxygen is essential to the passivation and hence, corrosion resistance of stainless steel. The dynamic breakdown and repair of the oxide film, requires constant supply oxygen. If oxygen levels are too low or become depleted, such as under a gasket or the result of biofouling, these areas will become anodic relative to the exposed surface. However, if the level of oxygen concentration is too high, the likelihood of pitting will increase, as the

local potential is shifted to more noble values where pitting can occur, by the presence of extra cathodic reactants [11]. These conditions also increase the rate of pit propagation after initiation [5].

4.5. Dissolved Chloride Concentration

The effect of chloride concentration on the pitting characteristics of various metals and alloys has been the subject of many studies [6, 7]. It has been the subject of interest due to its presence as a major constituent in seawater and its use as a biocide in potable water systems. The severity of pitting corrosion tends to vary with the logarithm of the chloride concentration of the bulk solution. Chloride is the anion of a strong acid and many metal cations are considerably soluble in chloride solutions. The chloride anion is relatively small and highly diffusive allowing it to migrate into crevices and existing pits. As stated previously, chloride ions break down the protective layer of Chromium oxide Cr_2O_3 by a competitive absorption mechanism in which chloride ions move into the metal oxide interface at the metal surface. This process continues until a critical potential, E_{pit}, is reached. This potential corresponds to the concentration of chloride required to displace the oxygen from the protective oxide layer [6, 7].

4.5.1. Forms of Chlorine in Water

Combined Chlorine is free chlorine that has combined with ammonia or organic amines and is essentially ineffective as a sanitizer [12].

Free Chlorine, also known as residual chlorine is present in water as dissolved gas (Cl_2), hypochlorous acid (HOCl) and/ hypochlorite ion (OCL^-). These three forms exist in equilibrium according to the equations:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

$$HOCl \rightarrow H^+ + OCl^-$$

The relative amounts of each are a function of the temperature and the pH of the solution. Figure 1 shows the effects of pH on the form of free chlorine in water at 25°C.

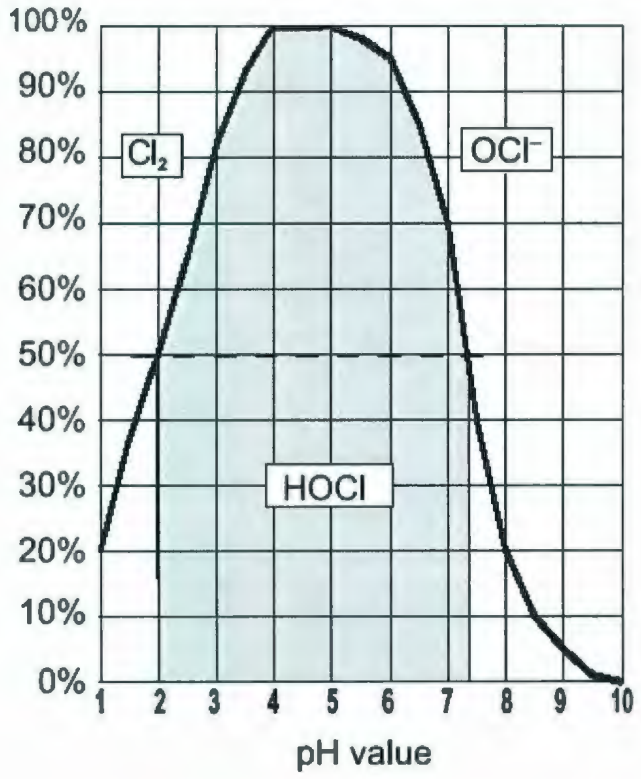

Figure 1 The effect of pH on the composition of Free Chlorine. (Source: *Forms of Chlorine in Water*, Edstrom Industries Inc., 2003)

At pH values of 5 to 7, as typically associated with potable water systems, figure 1 indicates that equilibrium will favor HOCl as the form of free chlorine. HOCl is the most powerful form of free chlorine making it most effective as a sterilizer at these pH values [12].

Total chlorine is the sum of the free and combined chlorine. In most potable water systems the concentration of ammonia or organic compounds is sufficiently low such that the total chlorine and the free chlorine are essentially equal.

4.5.2. Disinfecting

Before a new potable water system in put into service or after significant periods of no use, such as major maintenance or long outages, the addition of sufficient chlorine to achieve a minimum concentration of 25 ppm can be used to disinfect the system. Given the free chlorine concentration limits noted above, it would be assumed that concentrations of 25 ppm would be deleterious to the corrosion performance of the stainless steel. Tuthill [3] reports that the short-term exposure to the higher concentrations actually improves the corrosion resistance of the stainless steel. It is thought that this improvement is achieved by oxidizing any unoxidized material in the protective film. Tuthill also reports that published findings show for concentrations up to 25 ppm chlorine there was no general or localized corrosion for 31- to 32-day exposure.

4.5.3. Bacterial Control

As stated previously, chlorine is widely used for the biocide treatment of water. Chlorines effectiveness as a biocide comes from its ability to bond with and destroy the

outer surfaces of bacteria. With proper daily flushing of the distribution system and manifolds, effective levels of bacterial control can be achieved with 3-5 ppm free or residual chlorine in filtered domestic water [12]. Type 316L can be expected to be resistant to pitting corrosion in the 3-5 mg/l (ppm) range of residual chlorine [3].

4.6. Microbial Induced Corrosion (MIC)

As stated above, potable water is treated with additives, such as chlorine, to control pathogenic bacteria. These treatments also reduce and control bacteria that might initiate corrosion of stainless steel. Biocides are generally beneficial to the performance of stainless steel. However, there are instances where MIC occurred in potable water systems.

There are a number of reported cases in which water use for cooling or hydrostatic testing was not promptly drained and was the probable cause of MIC corrosion attack at the circumferential welds in the stainless steel piping [13,14]. In these reported cases, stagnant or low flow conditions prevailed.

Jack [15] states that MIC is perhaps the only mechanism that can perforate stainless steel piping in neutral aqueous service. Reports of penetration rates of 17 mm/year (0.7 in./year) in UNS 30800 welds have been documented. Perforation of 316L stainless steel weldments in piping with 5.5 mm (0.2 in.) wall thickness in industrial water systems under intermittent flow in four months has been described [13, 15].

A common feature of MIC is a preferential attack of some sort. Corrosion is often focused on the weld material or at the fusion line for the weld. Consistent with preferential

corrosion, pit surfaces are often described as dendritic, but the preferential attack of a single phase need not be a feature of MIC. Detailed studies of UNS 30800 weld specimens concluded that either ferrite or austenite could be preferentially attacked or they may corrode together, depending on a number of possible conditions [15]. Surface roughness defects caused by the welding process can contribute to the development and build up of biofilm. The metabolic activity of microorganisms within the biofilm causes MIC [16].

MIC has been known to occur in freshwater systems in the presence of significant concentrations of manganese. At these concentrations, a manganese containing deposit forms when chlorine is added. This deposit in normally benign, but in the presence of oxidizing bacteria such as gallionella, a self-sustaining corrosion reaction is initiated resulting in severe pitting [3]. This form of corrosion is uncommon but should be considered when raw waters contain significant amounts of manganese.

5. Factors Influencing the Pitting of 316L Welds

Welds in stainless steel have to be given special attention, as they are often most troublesome in piping systems prone to corrosion related failures. In addition to the variables that affect the corrosion resistance of the parent material, the welds are subjected to others that further complicate the issue of corrosion resistance.

5.1. Mechanical Factors

Mechanical factors are those related to the handling, preparation, welding and finishing of the final product. Cutting, drilling, grinding, for example will remove the passive film and possibly introduce foreign material to the metal and be the source of discontinuity in the re-passified film. For this reason, welding procedures for stainless steel stipulate that all tools used preparation, fabrication and finishing should be of similar material and be dedicated to use on stainless steel [5].

5.2. Thermal Contribution During Welding

The welding method, typically gas metal arc (GMA) or submerged metal arc (SMA), can have substantial metallurgical effects on the properties of the weldment. These effects are products of the heat input associated with the chosen method [17].

316L is a low carbon version of 316. The low 0.03wt% maximum carbon version is used for welded applications such as piping that are difficult to anneal in field installations. The purpose of the low carbon grade is to ensure that the heat of welding will not sensitize the heat-affected zone (HAZ) of the weld making it susceptible to intergranular

corrosion. The term sensitization refers to the condition that occurs when chromium carbide precipitate in the grain boundaries during cooling through the critical temperature range of 850 to 400°C. These chromium carbides reduce the chromium content of the areas adjacent to the grain boundaries and without sufficient diffusion from the grain structure, the available chromium drops below the critical 12% for pitting resistance [18].

316L may not be prone to sensitization, but intermetallic phases can precipitate in the HAZ. The intermetallic phase delta-ferrite is examined below. Welding changes the surface distribution of elements. These include oxygen, chromium, nickel, iron and manganese across the weld and the HAZ, with an adverse effect on the passivity of the surface layer. Under moderately oxidizing conditions, weld metal austenite may suffer preferential corrosion in alloy-depleted areas. This attack is the consequence of microsegregation or coring in weld metal dendrites [5].

5.3. Weld Root Physical Characteristics

The weld root has physical features that can promote the initiation and development of pits. The surface of the weld contains crevices that are produced by the deposit of filler material. The presence of microporosity, as evidenced by a cast structure [5], in the weld metal provides favorable sites for the initiation of corrosive attack.

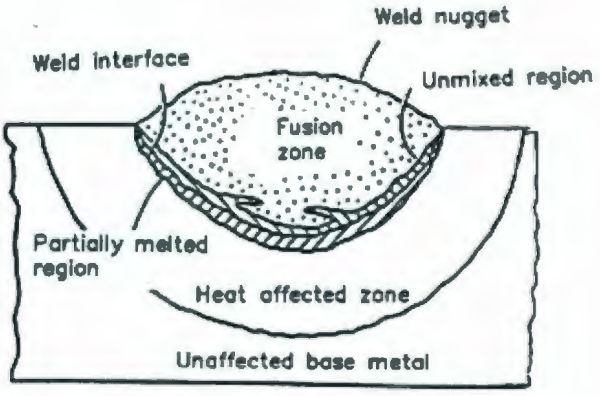

Figure 2 Diagram of a weld depicting different zones. (Source: Corrosion of Stainless Steel Weldments, ASM Metals Handbook, Vol. 13, Corrosion, American Society of Metals, Ohio, USA, 1998)

When welding stainless steel, the proper filler material must be used. This material should be such that the properties of the parent material are at least maintained if not exceeded [5]. These include metallurgical and corrosion resistance properties. The concept of using an "over alloyed" filler metal has been developed in order to counteract the effects of segregation. The selection of an appropriate filler metal, which is over alloyed compared to the base metal, ensures that the concentrations of the major alloying elements are sufficient to provide superior corrosion resistance to that of the base material. Not only does the material have to be compatible for strength and toughness, but also to control galvanic differences between the parent material and the filler material. Over alloying can intentionally create a galvanic difference between the weld and parent material. The reason for doing this is to prevent the corrosion of the weld bead by having the filler metal corrosion potential be noble to the parent material. The practice of selecting a filler material that is over alloyed has shown that the critical pitting

temperature of the weld metal exceeds that of the base material [19]. This practice cathodically protects the welds. Given the large area ratio between the anode and cathode, this can be applied without risk to the parent material [4].

5.4. Manganese Sulfide

If there is a high concentration of Fe and Mn ions (>10ppm), adding chlorine to potable water is one way to facilitate the precipitation of iron and manganese so they can be filtered out. In environments that are high in manganese, black deposits of iron hydroxide and manganese hydroxide form on the pipe walls. This deposit is benign to stainless steel and stainless steel welds, however these deposits have led to corrosion in the HAZ in the presence of free chlorine. This corrosion is known as Under Deposit Corrosion (UDC) and occurs in fresh water with low chloride concentration in the HAZ where the heat tint scale has not been removed [3, 20].

Pitting was found to have occurred in the heat-tinted area but not in the weld or clean parent material although a black manganese deposit covered all three areas [3].

5.5. Delta-Ferrite

Delta-ferrite is a body centered cubic (bcc) structure that is found in austenitic steels. Its formation is a function of the chemical composition of the parent and weld metal, the heat input during welding as well as the cooling rate. The amount of delta-ferrite is controlled as its presence in an austenitic weld (2 - 10%) helps to prevent hot cracking of welds. While beneficial to the mechanical properties of austenitic steels, the presence of delta-ferrite is detrimental to corrosion performance as it is preferentially corroded in

aggressive environments [5]. In both casting and welding applications, solidification modes include austenitic, austenitic-ferritic, ferritic-austenitic and sometimes ferritic. The ferritic-austenitic mode of solidification is preferred as the ferrite has a higher solubility of weld slag elements than the austenite and this solidification mode is less susceptible to hot cracking than the other modes. In the ferritic-austenitic weld, ferrite solidifies first, and austenite forms between the ferrite dendrites. The austenite subsequently grows into the ferrite, resulting in a significant decrease in the volume fraction of ferrite. At room temperature, the weld is substantially austenite, with a small volume of retained ferrite.

The competition between ferrite-promoting elements and austenite-promoting elements can be described by the chromium and nickel equivalents. The chromium equivalent takes into account those elements promoting ferrite formation, while the nickel equivalent accounts for those elements promoting austenite formation. Since 316L is an austenitic stainless steel, there must be enough chromium present to form the stable chromic oxide layer, which gives the steel its stainless characteristics, and enough austenite-forming elements to stabilize the crystal structure as austenite. There are several commonly used chromium and nickel equivalents, but the equations developed by Hammar and Svensson as reported by Collins [21], show an excellent correlation between composition and solidification mode, especially for austenitic stainless steels.

The Hammar and Svensson equivalents are:

$$Cr_{eq} = Cr + 1.37\ Mo + 1.5\ Si + 2\ Nb + 3\ Ti$$

$$Ni_{eq} = Ni + 0.31\ Mn + 22\ C + 14.2\ N + Cu$$

Where eq = equivalent, and all elements are reported in weight percent.

Using these equations, the solidification mode can be predicted by the ratio of Cr_{eq} / Ni_{eq}. For Cr_{eq} / Ni_{eq} < 1.5, the solidification mode is austenitic or austenitic-ferritic. For 1.5 = Cr_{eq} / Ni_{eq} = 2.0, solidification is ferritic-austenitic, and for values of Cr_{eq} / Ni_{eq} > 2.0, solidification is ferritic. Acceptable welds have no slag, and will be very slightly magnetic, indicating some retained ferrite. The higher the Cr_{eq} / Nieq, the higher the propensity for ferrite formation [21].

An increase in ferrite translates to a decrease in corrosion resistance, but the delta-ferrite content at which corrosion resistance is affected significantly has not been well established [21].

In percentages of 5% or less, the delta-ferrite appears as islands in the alloy matrix and those on the metal surface are attacked. If the percentage of delta-ferrite is greater that 8-9%, a continuous network is formed favoring corrosion of the weld deposit [22].

Punjar et al. [23] states, it has been reported that delta-ferrite has an important bearing in determining electrochemical parameters and that its role is equivalent to that of chromium. The exact role of delta ferrite in affecting the passivity of the weld metal is not known.

Punjar et al. [23] also demonstrated that as the heat input increased, the time to the final breakdown of the passive film decreased rapidly, which is attributed to the fact that with an increase in heat input, the ferrite particles gradually become coarser. The coarser particles result in a more unstable passive film at the matrix and particle interface.

Dissolution of such a passive film becomes easier, a fact that has been amply supported by the literature where the rate of reductive dissolution of the passive film in the acid solution has been correlated with the presence of second-phase particles.

5.6. Heat Tint

Heat tint refers to an oxide layer that develops alongside the welds in stainless steel during fabrication. It is the result of inadequate inert gas shielding of welds allowing oxygen to access the metal surface causing heat tinting of the weld roots.

This chromium oxide layer, which is not to be confused with the naturally occurring ultra-thin 20 Å layer that gives stainless steel its corrosion resistance, is a thicker scale with a mixture of iron, nickel as well as other oxides. It is understood [24] that this colored metal oxide film can in various environments affect the in-service corrosion resistance of welded stainless steel joints. It is the service environment that determines the severity of this affect. In service corrosion attack on heat-tinted weld roots is most likely to occur in aqueous environments. Any degree of heat tint may be unacceptable if the oxide can compromise service cleanliness.

During heating, the natural transparent passive layer grows in thickness as chromium diffuses out of the base material forming heat tint colours ranging from a pale straw to a dark blue oxide scale. The dark blue heat-tint oxides are most susceptible to localized corrosion attack [24, 29]. The heat-tint scale consists of a heterogeneous oxide made up of the metallic elements of the stainless steel. The properties of the oxide surface depend on the following:

- Time and temperature of the thermal exposure.
    - Increased time at elevated temperatures allows for increased diffusion of chromium.
- Composition of the atmosphere in contact with the hot metal surface.
    - An inert backing gas or electrode coating is used to remove or prevent oxygen from coming in contact with the metal surface.
- Chemical composition of the base metal beneath the heat-tint oxide.
- Physical condition of the surface (contamination, roughness, thermomechanical history) prior to heat tinting, and
- Adherence of the heat-tint oxide to the base metal.

The heat-tint scale is a poor barrier to corrosive media due to defects and stresses within the oxide [25]. This lack of a coherent passive oxide film on the weld can result in localized corrosion at weld locations in certain aggressive environments. Possible corrosion mechanisms include pitting corrosion, crevice corrosion, and in raw water or wastewater environments, MIC.

During the formation of heat tint, chromium diffuses out of the base metal and into the heated zone since chromium is more readily oxidized than iron in the steel. The depth of the diffusion zone extends as far as the heat will allow the diffusion to take place. This diffusion of chromium into the scale leaves a thin layer with reduced chromium content just below the heat tint scale. Since chromium is responsible for giving stainless steel its corrosion resistance, this area would now have reduced resistance to localized corrosion

particularly in the presence of oxidizing acid solutions. Corrosion that would not occur elsewhere can initiate in the depleted areas unless the heat tint and the resulting thin depleted area are prevented and/or removed [26, 27].

5.6.1. Acceptance Criteria for Heat Tinting

There is on-going debate [24] as to acceptable levels of heat tint on stainless steel welds. Two major topics of debate that challenge the stainless steel and user industries are an interchangeable graphical illustration that depicts different levels of oxidation and an understanding and agreement on acceptable levels of oxidation for different environments. The more severe the service environment is, the lower the tolerance for the presence of heat tint.

The American Welding Society has published AWS D18.2: 1999, Guide to Weld Discoloration Levels on Inside of Austenitic Stainless Steel Tube that contains a graphical illustration of ten (10) welds with varying degrees of heat tint. This standard is included in part in Appendix D for reference. The degrees or levels of oxidation are represented by sequential numbers and to be used to identify oxidation levels in user applications.

Welding of 316L stainless steel requires purging by an inert gas both before and during welding. Since, in field installations, 100% effective inert gas purging is difficult to achieve due to local circumstances around the weld, there are varying levels of oxidation that occur. Potable water systems, for example, are typically placed in service in the as-welded condition and grinding, pickling or other means of removing heat tint are either not acceptable or not feasible. As a result, the practice is to examine completed welds

and determine if the level of oxidation is below an acceptable limit. If the oxidation is too severe, the weld is removed and redone. The question is, how does one evaluate the severity of the heat tint and how severe is too severe? Internal inspection of butt welds in piping is difficult and the interpretation of the results is subjective.

5.6.2. Repairing Heat-tinted Surfaces

The corrosion resistance of areas that have been heat-tinted can be restored by means of mechanical and/or chemical cleaning. As mentioned above, there is a thin layer of steel below the heat-tinted area that has a reduced content of chromium. To prevent the onset of corrosion of this surface it has to be removed. This can be done mechanically by; grinding, brushing, blasting or it can be removed chemically by a process known as pickling.

Grinding is a common practice for the removal of defects such as; shallow surface marks, weld spatter, arc strikes and other conditions. If improperly cleaned, a surface can become more susceptible to corrosion than the original heat-tinted surface. Grinding or brushing operations can smear and imbed the heat-tint oxide on the surface, or expose the Cr-depleted layer without completely removing it. An example of improper cleaning is the pitting of a stainless steel weldment caused by stainless steel wire brushing. In this case, it is believed that a stainless steel brush of different composition was used to clean the welds, leaving deposits of inferior material or the removal of the depleted surface layer was incomplete [5].

The two main constituents of stainless steel pickling products are nitric and hydrofluoric acids. As such, care has to be exercised in the use of pickling agents both from an environmental perspective and metallurgical point of view. If acid contact times with the stainless steel as well as the final rinsing procedures are not properly controlled, corrosion can be initiated in the treated areas. It is important that all traces of pickling products, pickle residues and contamination are completely rinsed from the surface of the steel parts to achieve a fully corrosion resistant and stain free surface.

In some applications involving on-site stainless steel pipe welding, removing all heat tint oxides after welding is very difficult to carry out, even after using appropriate gas purging. During closure of stainless steel pipes by welding heat tints are sometimes detected during inspection in areas that are impossible to access, such as inside circumferential butt welds on smaller diameter pipes. These areas are inaccessible by mechanical means of cleaning and chemical cleaning requires large volumes of acid solutions to be transported to job sites and the disposal can be difficult as regulations can be restrictive on such chemicals. Cleaning of external pipe butt weld surfaces to restore the corrosion resistance can be carried out with relative ease. However, removal of undesirable heat tints on weld root surfaces can be difficult, time-consuming and expensive, particularly at remote job sites.

5.7. Factor interaction

It is clear there are a number of factors that can contribute to the onset of corrosion of stainless steel welds. Each of which requires consideration in the design of corrosion

resistant piping systems. It is quite possible, and is most likely factors contributing to corrosion do not act completely independent. Heat tint scale has a direct influence on the corrosion resistance of the surface. When present, it can enhance the contribution to pit initiation of other factors such as MIC or the presence of delta ferrite. Tuthill and Avery [26] state that research has shown that heat tint removal enhances the resistance to microbiological induced corrosion. As stated above, Tuthill [3] reports that manganese deposits, can lead to crevice corrosion in the heat-tinted area of circumferential welds. Pitting was found to have occurred in the heat-tinted area but not in the weld or clean parent material although a black manganese deposit covered all three areas. This is an indication of the reduction in corrosion resistance of the heat-tinted steel as compared to the unaffected steel.

6. Case Studies

Below are three cases from the author's experience demonstrating the deleterious contributing effects of heat tint scale to the pitting failure of 316L stainless steel welds.

Case 1: Circumferentially butt welded 316L used in potable water service.

Piping runs on an offshore platform are seldom straight and simple. As a result, field fits can be complex creating difficulty for welding. If backing gas cannot be properly contained, oxygen ingress will increase the degree of heat tint left on the weld root and adjacent surface.

In this particular case the pitting in the weld was attributed to biological activity. The pit had propagated through the weld metal to the exterior of the pipe resulting in a pinhole leak. These types of failure occurred through out the system resulting in an engineering decision to replace the 316L material with a fire resistant polymer material.

According to Tuthill [26], the threat of MIC can be compounded by heat tint scale. The welding specification for this piping system did not provide for any post weld cleaning. Other stainless steel piping systems on the platform all had post weld cleaning requirements. Given the conditions under which the welding was completed and the lack of cleaning procedure, the presence of heat tint scale is probable, contributing to the failure by MIC.

Case 2: High Pressure Mist Fire Suppression System.

This piping system is used for suppression of fire in the living quarters aboard an offshore installation. The pipe work required passing through a number of bulkheads and walls. The difficulty of performing field welds was clearly evident in this system. This system was fabricated using 316L couplings to join 316L pipe sections. In addition to alignment problems there was evidence of difficulty faced by the welder. Start and stop marks, weld spatter, and a rough weld profile demonstrated the poor weld quality.

The failure of the joint was a narrow pit that had penetrated weld metal. In addition to the poor weld quality, the coupling joint provided a natural crevice that was internally covered by a severe heat tinting.

Case 3: 316L Stainless Steel Tote Tank

These tanks are used to transport various chemicals and liquids between shore and offshore production platforms. During an annual inspection of one of these tanks, pitting corrosion was noted in the vicinity of a longitudinal weld. The environment to which the tank internal surface was exposed is unknown. Given the volume of the tank, applying backing gas during construction was not practical. Post weld cleaning by mechanical means was clearly evident but has not completely removed the heat tint oxide. The weld metal was free of any corrosion. The tinted areas contained light pitting but the largest pits were noted as being along the edge of the lightly tinted surface adjacent to the weld.

7. Experimental Procedure

Corrosion tests were performed in accordance to ASTM G48-03 method A to examine the pitting behavior of the weld metal and heat affected zone as a function of the level of oxidation.

The corrosive media used in this experiment was made using distilled water and reagent grade chemical Iron (III) Chloride. The Environmental Lab of the Faculty of Engineering and Applied Science supplied the Type IV water, as defined by ASTM D1193 [31].

An immersion test was chosen to examine the pitting behavior of welded stainless steel as a simple examination of the relation between the degrees of heat tint and pitting corrosion was desired. Polarization experiments would have only provided a similar examination as it has been shown [5] that the results of such work are simple for the development of understanding of pitting behavior. The heterogeneity of welded samples would prove to be detrimental to the determination and comparison of data acquired through potentiodynamic measurements. Recorded corrosion activity would be difficult to correlate to the features of a welded sample simply due to the number of variables associated with welding. When considering heat tint, the quantification of affected area and the severity of effect is a subjective judgment. In addition to the varying heat tint scaling, the weld metal made up a significant portion of the corrosion sample. The weld deposit varied in size and features. Potentiodynamic experimental results would be very difficult to reproduce.

Visual examination, photographic reproduction as well as pit depth measurements were used to characterize the pitting corrosion of the different samples.

7.1. Apparatus

The experimental set-up consisted of the following; a beaker large enough to hold a volume to provide a volume to specimen surface ratio of at least 5 mL/cm^2 of 6% by mass ferric chloride solution, a constant temperature bath maintained at 22±1°C and a sample holder made of PTFE. An ultra sonic cleaner was used for post immersion cleaning of the samples. Microscopic examination was carried out using a Wild-Leitz optical microscope.

7.2. Sample Preparation

Sample preparation consisted of cutting samples from four pipe coupons welded according to the specification in Appendix A. The pipe, or parent material, was 316L stainless steel as per the mill certification in Appendix B and the filler material used to produce the welds was designated ER316L as per the certificate of compliance in Appendix C. The 99.99% pure argon purging of the pipe was varied for each coupon to produce varying oxidation or heat tint. This was accomplished by reducing the flow rate of the argon backing gas. The purpose of varying the purging gas was to simulate the conditions that could occur in a field installation in which the gas setup may be inadequate for full gas flow rates. In addition to the oxygen that would ingress, the atmospheric air would also contain moisture. While these variables could not be quantified in this circumstance, the results represented in-the-field welds. The full flow

rate of the backing gas used was 45 CFH (cubic feet per hour). The flow rates on subsequent coupons were 30, 15 and 0 CFH. These levels of backing gas along with the natural variances in welding such as welder speed and position produced a full range of heat tinting from very clean to dark blue oxide layers. Samples from Group 1 had the oxidation and chromium depleted zones removed by mechanical means (grinding) to produce samples with minimal visible oxidation present.

During sample preparation, efforts were taken to not alter the as-received condition of the sample surfaces, as this would produce more meaningful results by duplicating as-installed conditions found in the field.

Samples were cut from the pipe coupons by band saw and the edges deburred using a dedicated grinder to prevent possible contamination. The cut and ground edges as well as the back of the samples, which was the outer diameter of the pipe, were covered with an epoxy to prevent corrosion of these surfaces. Photographs were taken of each sample for comparison after testing.

Prepared samples were then immersed in corrosive medium for a period of 72 hours as per ASTM G48.

7.3. Evaluation

Evaluation of the pitting of each of the samples was carried out in accordance with ASTM G1-03 [30] and G46-94 [33]. Corrosion products were removed by scrubbing with a stiff bristle nylon brush followed by ultrasonic cleaning and samples were stored in a dessicator until evaluations could be completed.

Visual examination of the sample surfaces was carried out in ordinary light with a low powered magnifying glass to determine the extent and relative location of pitting. Photographs were also taken at this point for comparison to photos of the non-corroded surfaces.

Pit density, size and the depth of the pits were evaluated using optical microscopy. Depth measurements were made using the calibrated movement and focusing of the microscope. Mass loss measurements were attempted, however most samples had corrosion at the metal - epoxy interface making the results of mass loss calculations invalid.

8. Results and Discussion

The purpose of the tests performed was to determine if an increasing susceptibility to pitting corrosion could be linked in proportion to the severity of heat tint. The following describes the experimental observations, which are followed by discussions for each of the sample groups, then in general for all samples. Where applicable, hypotheses have been developed to explain some of the unexpected results. Comments on experimental issues and the acceptance of heat tint scale are also presented. Pictures of particular samples are included below for illustration but the reader is encouraged to refer to Appendix E, which contains pictures of all weld samples used for immersions testing before and after the experiments.

8.1. Experimental Observations

Table 1 below contains measurements of sample pits.

Sample Group	Sample Number	Location	Pit Description	Pit depth (mm)			
1 (No tinting)	5	Weld	Single pit in weld metal.	N/A*			
2	1	-	-	N/A**			
	2	-	-	N/A**			
3	1	HAZ/PM	Random selection of smaller pits	0.008			
		HAZ/PM	Largest pit in HAZ	0.025			
		HAZ/PM	Second largest pit	0.010			
		Weld		0.015	0.014	0.010	0.011

	5	HAZ		0.010	0.05		
		Weld		0.025	0.021	0.020	0.018
	6	HAZ		N/A**			
		Weld					
	7	HAZ		N/A**			
		Weld	Single Pit	0.026			
		PM		0.003			
	8	HAZ		0.005			
		Weld	Minimal pitting in weld metal	0.003	0.005	0.003	
4	2	HAZ/PM					
		Weld					
	4	HAZ/PM					
		Weld					
	5	HAZ/PM		0.015	0.012	0.012	0.014
		Weld	7 pits in total	0.028	0.030	0.031	0.025
* Narrow pit opening made measurement impossible. Could not focus on the bottom of the pit. ** Pit depth indistinguishable from surface roughness							

Table 1 Sample pit depth measurements

8.1.1. Sample Group 1

Specimens from the first group exhibited good corrosion resistance. These specimens had been welded according to specification with full flow rate of 40 CFH backing gas and mechanically cleaned by grinding to limit the appearance of heat tint on the surface. There was no visible corrosion of theses specimens with two exceptions. It can be seen in Figure 3, specimen 1-5 had developed a deep pit in the weld metal, around which there was rust coloured staining. Post experiment examination of the pit had removed the staining and is not visible in the photo above. The iron from which the oxide was

produced may have come from the grinding tool used to remove the oxide scale. Specifications for the welding of stainless steel require environmental control that includes the use of dedicated tools to prevent corrosion caused by contamination.

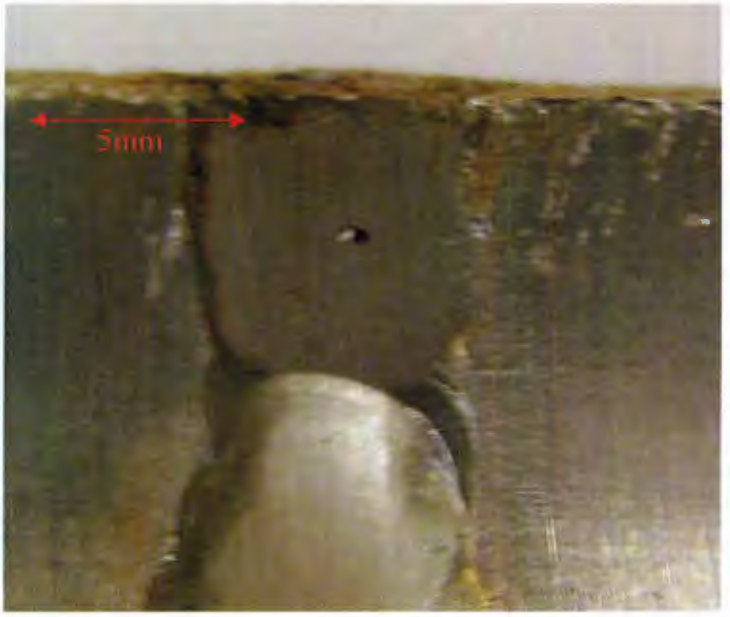

Figure 3 Sample 1-5 showing single pit in the weld metal

Sample 1-7 had light pitting at the weld deposit edge. This example of pitting demonstrates the influence of geometrical features on pitting behavior of welded steel. The edge of the weld deposit was a sharp discontinuity on the smooth surface of the pipe producing a site where pitting could initiate.

8.1.2. Sample Group 2

The second group of specimens was created with no purging or backing gas during the welding process. From the point of view of evaluating the corrosion resistance of stainless steel welds, these are not realistic candidates, as the condition would warrant removal of the weld and the joint re-welded. Without the use of backing gas, the weld root in these samples was extremely poor quality. Any weld deposit was cut out prior to immersion testing. This affected the corrosion performance of the specimens by limiting

any of galvanic differences found over the specimen surfaces. However, the oxidation that resulted on the parent material of these specimens was useful for evaluating pitting resistance of the HAZ.

Despite the heavy tinting of these specimens there was very little pitting found in the tinted areas. The most severely tinted area had a grey coloring and when exposed to the corrosive medium exhibited what appears to be general corrosion within that area. Once the area became active it may have cathodically protected the rest of the sample.

8.1.3. Sample Group 3

These samples were welded using a flow rate of 30 CFH backing gas. Pitting of the weld metal varied in density and depth. This group of specimens exhibited the most severe pitting of the parent material. The pits were found in the clean parent material and at or near the HAZ limits while areas of heavy tinting were not corroded at all.

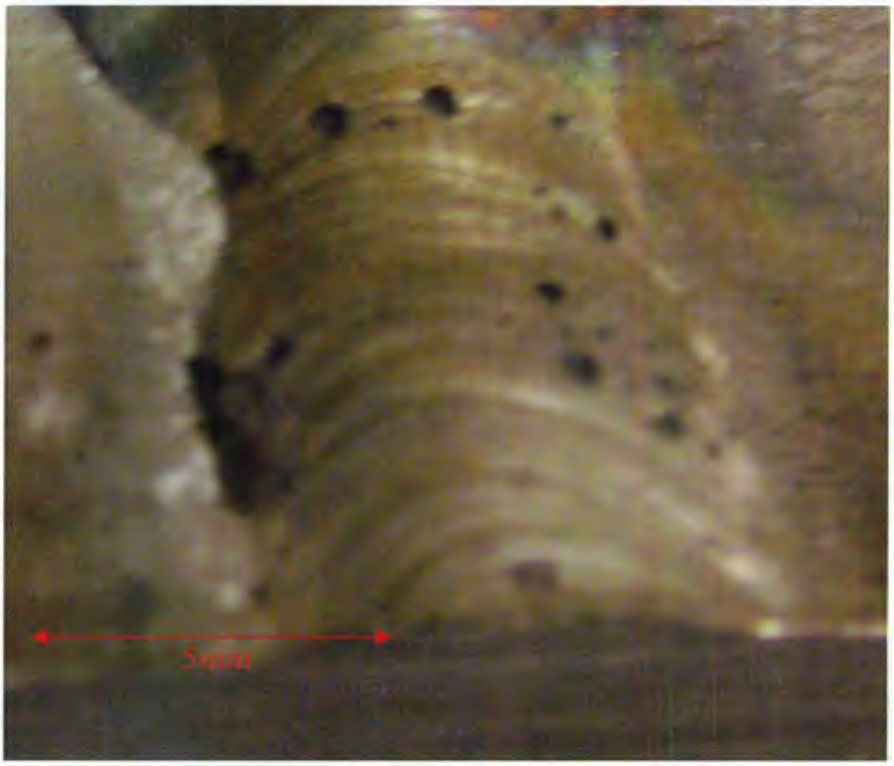

Figure 4 Sample 3-1 Pits coalesced to form crevice at weld edge

Sample 3-1 experienced heavy pitting at the weld metal edge such that the pits developed into a crevice as per Figure 4. Pits were found in the weld metal primarily in a location of a start/stop location as indicated by heat tint pattern across the weld bead. The largest of these was 0.015 inches or 0.381 mm deep. Sample 3-5 also showed heavy pitting of the weld metal.

Eight samples were cut from the original weld coupon. The five immersion samples from this group would have been adjacent to each other in the order of 3-5, 3-6, 3-7, 3-8 and 3-1. As stated above 3-1 and 3-5 showed significant pitting of the weld metal while 3-6, 3-7 and 3-8 showed relatively few pits in comparison. The difference in pitting behavior of welded samples from the same coupon and exposed to the same corrosive media is likely the result of metallurgical differences in the weld that are produced during the welding process. In section 5.5 the effects of delta ferrite on the corrosion resistance of welds was reviewed. Other secondary phase precipitates as well as delta ferrite may have produced metallurgical condition that promoted the corrosion of the weld metal in the areas from which samples 3-1 and 3-5 were cut.

3-6 developed wide deep pits at the outer visible limits of the HAZ.

In sample 3-5 and 3-8, the regions of pitting cross from the HAZ limits into heavier tinted areas. It was noted that there were mechanical marks, which the pitting followed across the HAZ. These mechanical marks are likely rolling marks from the fabrication of the pipe.

There are areas of heavy corrosion in these samples at the metal/epoxy interface. These areas of corrosion were ignored in the analysis.

8.1.4. Sample Group 4

Samples from the fourth and final group were fabricated using 15 CFH backing gas flow rate. The heat-tinting in this group had similar patterns of colour distribution and intensity as the previous group. One significant difference was the size of the heat-tinted zone. The outer limits of the coloured surface were 10 to 30% further from the weld root as compared to group three. This group demonstrated similar corrosion behavior as those from group three within the HAZ and parent material. The HAZ had little evidence of pitting corrosion. The parent material exhibited pitting in clusters. The pitting of the weld metal in this group was the most severe observed. The depth and size of the pits was significantly larger in this group. With reference to Table 1, it can be seen that the depth of the pits in the weld for Group 4 were approximately twice as deep as those measured in Group 3.

8.1.5. General Observations

Based on a comparison of the pitting performance between the samples in group one and the others, the corrosion resistance of welded 316L stainless steel is negatively affected by the presence of heat tint scale. In terms of a general trend, pitting occurred at the visible outer boundary of the HAZ, the clean parent material and within the weld metal.

The corrosion observed at the HAZ limits and clean parent material occurred in dense clusters that followed the contours of the visible heat tint oxide. The density of the pit

clusters decreased becoming isolated pits as the distance from the weld nugget increased. Pit depth was limited, generally having no discernable depth to the naked eye.

The pitting in the tinted areas was minimal with some samples not exhibiting any pitting in these areas. Pits that did develop in these areas exhibited greater depth and width than those in the HAZ limits.

Pitting of the weld metal varied from group to group as well as from specimen to specimen. This was particularly noticeable in sample group 3. The severity of pitting corrosion noted in the weld nugget appeared to be proportional to the size of the heat-tinted area. Samples from group 4 had a larger heat tint affected area and more severe pitting than the samples from group 3.

8.2. Pitting Behavior of Tinted Parent Material

According to literature [24, 25, 29], heat tint oxide is a poor barrier to corrosive media due to defects and stresses within the oxide. Boulton [24] states that straw and pale blue oxide films (light tinting) are relatively resistant to localized attack. It would be expected then, that the greater the degree of tinting, the more pronounced the deleterious effects of these defects and stresses would be. In other words, the greater degree of heat tinting or oxidation, the greater degree of pitting corrosion, exhibited in density, depth and/or size, could be expected. However this was not observed in this study. In all of the specimens that exhibited pitting corrosion in the parent material, the pits were generally found in dense clusters in areas of light tinting or areas along the boundaries of visible tinting and through out the 'clean' parent material. Areas of heavy oxidation exhibited an apparent

better corrosion resistance than areas of light oxidation. This would seem to be in contradiction to Bolton's statement. Possible explanations are presented below.

Heat tint oxide is described [25] as being incoherent, providing locations of exposure to the chromium-depleted layer resulting in pit initiation. At the limits of the HAZ where the temperature is high enough for diffusion of chromium, there would be locations of chromium depletion in the surface layer adjacent to chromium enriched oxide layers [11]. This description is supported by the observed pits in areas of light heat tinting where the initiation of excessive oxidation likely occurs at discrete points. Specimens 3-1, 3-5, 3-8, 4-2 and 4-5 all display dense shallow pitting in the areas just described. The locations that exhibited pitting are most likely areas in which the protective chromium oxide layer was compromised enough to facilitate pit initiation but the depth of diffusion of chromium below the oxide layer was limited to a thickness that would only allow the establishment of shallow pits in the time frame of the experiment.

One possible explanation for the absence of pits in the more severe heat-tinted areas could be the severity of the tinting itself. The heavier tinting is the result of greater oxygen availability resulting from lower levels of backing gas used to produce the samples. As stated in section 4.6, the more heat that is available, the deeper the diffusion of the chromium. The increased availability of chromium and oxygen may have resulted in an oxide layer that is thick enough to compensate for any incoherencies in the oxide, thus protecting the depleted layer of stainless steel below the heavy film. This is supported by the observation of samples from group 2. These were produced without any backing gas and completely covered in heavy heat tint scale when exposed to the corrosive test

solution. With the exception of grey tinted areas adjacent to the cut out weld, the pitting on these samples was barely visible to the naked eye. For the seventy-two hour exposure the red to blue or heavy heat tint oxide remained intact.

When pitting initiated in the heat-tinted zones, it was deeper, wider and of a lower density than the pitting noted in the untinted parent material. The picture below shows an example of this from the sample 3-6.

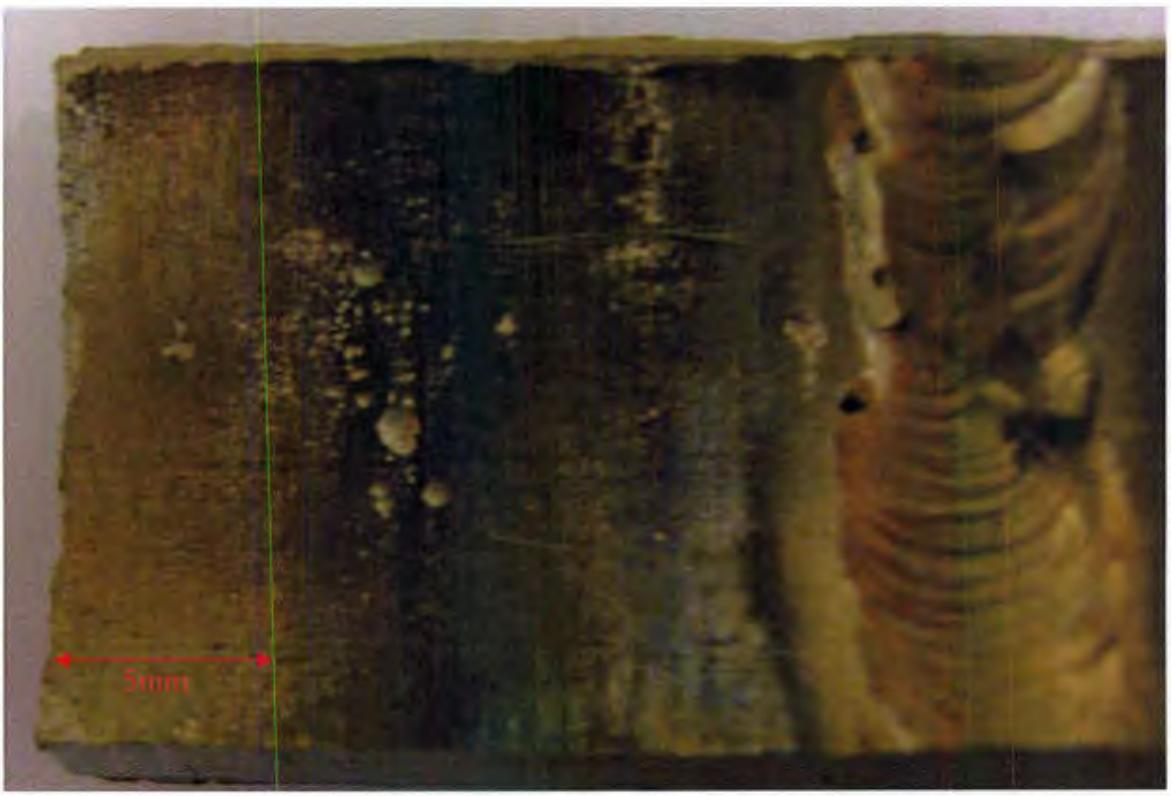

Figure 5 Significant pitting occurs at the outer limits of the HAZ

The deeper/wider pits are the result of greater chromium diffusion that had taken place below the oxide layer. The exposure time of the experiment in accordance with ASTM G48 was seventy-two hours. If the exposure time had been longer it is possible that severe

pitting would have been found throughout the areas of heavy tinting as the oxide layer broke down.

Another possibility for the locations of pits could be the galvanic differences over the sample surfaces. The chromium enrichment [29] at the metal/oxide surface coinciding with progressively darker heat tint oxides could increase the nobility of these areas relative to the clean surfaces of the parent material, surfaces with low heat tint and the surface of the weld metal. The density of the initiated pits could also suggest the cathodic reaction required to sustain the pitting may not be immediately adjacent to the developing pit but is provided by the tinted surface. This is supported by the observation that tinted surfaces do not exhibit the same degree of pitting as the non or light tinted areas and that pitting corrosion is concentrated at the boundary of these areas. This is illustrated in the picture below. Note the pit cluster to the right at the boundary of the visible heat tint oxide.

Figure 6 Pitting occurred in the weld and at the HAZ limits.

The corrosion of the parent material is also influenced by the limited anode to cathode ratio. The larger the cathode in a galvanic corrosion cell the greater the corrosion rate. In a piping system, the parent material would be a large anodic area unlike the limitations of sample sizes found in these lab experiments.

Turner et al. [29] attempted to measure the galvanic differences between heat-tinted specimens but after 20 hours did not observe any measurable effects. Galvanic corrosion requires the dissolution of a metal species into the electrolyte. It was noted in the experiments undertaken in this study that heavier heat tint oxides can remain intact over a 72 hour period in a corrosive media. If the heat tint oxide remained intact for the 20 hours in Turners experiments, the specimens used may have remained in a passive state. The electrolyte used in Turners experiment was naturally occurring water from a

mineshaft that contained a low concentration (25 ppm) of halides, which over the time frame of the experiment, may not have been sufficient to breakdown the passive film.

Based on the observations of pitting in the parent material, areas of light oxidation (straw and pale blue) have an apparent low resistance to pit initiation but a greater resistance to pit growth. At these locations the heat available from welding was only sufficient to initiate diffusion of the chromium both within the metal and on the surface resulting in an incoherent oxide film, which would promote pitting initiation. Due to the limited heat available, the diffusion below the surface only developed a thin chromium depleted layer. Within the time frame of the experiment, the heavy oxidized surface demonstrated a greater resistance to initiation but if the heavy oxide was compromised a lower resistance to pit growth was obvious as demonstrated by the depth and size of the occurring pits. The heat available near the weld would have promoted a deeper diffusion of chromium to the surface where it could oxidize resulting in a thick heat-tinted layer. The thickness likely compensated for any incoherencies in the film providing corrosion resistance during the experiment. The resulting deeper diffusion resulted in a less corrosion resistant metal.

8.3. Pitting of Weld Metal

Field experience, see section 5, has demonstrated that pitting corrosion leading to failures often occurs in the weld metal when heat tint is present. This tendency of preferential weld corrosion was observed in this study. The pitting observed in the weld metal not only varies from group to group but also varies between samples within the groups.

For the specimens from group one, care was taken during the welding to ensure a clean weld. The welds were then ground creating a smooth finish on the weld metal eliminating crevices and reducing the porosity of the weld surface. Despite the efforts to produce corrosion resistant welds, two incidents of corrosion were noted. The first was a single pit believed to have been initiated by a foreign deposit. The second was a crevice formed by the weld bead that served as an initiation point. Despite these exceptions, the clean welds of group one demonstrated excellent corrosion resistance.

Group two was not used to evaluate weld bead corrosion. The resulting welds were of such poor quality in the absence of backing gas they would not have been representative of acceptable field welds.

Sample groups three and four exhibited pitting of the weld metal in the presence of heat tint. Compared to sample group one, there is clearly a deleterious effect of heat tint oxide on the corrosion resistance of the weld metal. Comparing sample groups three and four, there is also a relation between the size of the heat-tinted area and the severity of pitting in the weld metal. Sample group four, which was produced with a lower backing gas flow rate, had a larger heat-tinted area and larger, deeper pits than group three. As stated earlier, the corrosion rate is proportional to the cathode to anode ratio. The larger the cathodic area, the grater the corrosion rate will be. The observed corrosion in sample groups three and four support the hypothesis that the influence of heat tint oxide on the corrosion of stainless steel weld metal is galvanic in nature.

If heat tint is present, there appears to be a change in the galvanic potential between the parent material and the weld bead. Filler material, as stated in section 4.3, is often

designed and chosen to produce a protective galvanic potential difference to cathodically protect the weld metal. When present, the heat tint appears to shift the nobility away form the weld bead making it susceptible to corrosion.

It was noted during examination of the welds, adjacent samples exhibited differences in corrosion behavior. As stated in Section 4.5, Punjar et al. [23] explained that as the heat input increased, the time to the final breakdown of the passive film decreased rapidly. Sample 3-1 and 3-5 have heavy pitting in the weld metal at locations that were heavily tinted and appeared to be start-stop locations. This would have resulted in excessive heat being applied to the metal in these locations. As stated earlier, this likely resulted in the formation of secondary precipitates and excessive delta ferrite creating locations of preferential corrosion. The description given by Punjar is a plausible explanation for the observed pitting.

8.4. Comments on AWS D18.2: 1999

AWS D18.2: 1999, Guide to Weld Discoloration Levels on Inside of Austenitic Stainless Steel Tube is an example of a graphical tool for the assessment of heat tinting. While this tool offers some continuity of interpretation of heat tint levels, there is a significant degree of subjective interpretation. The welds made for these experiments were compared to this guide. The first noted difficulty in interpretation was the difference in heat tint patterns. The various colours of tinting in the samples created here did not follow any discernable pattern of distance from the fusion boundary. Next, the interpretation of the colour of the tint is subject to lighting conditions. If welds in a pipe

are to be inspected by closed circuit television camera or other similar equipment, there is a great reliance on the skills of the inspector. There is no guarantee that another inspector will arrive at the same conclusion.

8.5. Limitation in Evaluating the Pitting Resistance of Welded Samples

ASTM G48 provides the means to examine the effects of alloying additives, heat treatment and surface finishes on the pitting corrosion resistance of stainless steels. Heat-tinted stainless steel welds are very heterogeneous in terms of surface condition. The weld bead adds a second, often different, material to the specimen. Difficulty in controlling welding to exact tolerances makes duplication of specimens for comparison practically impossible. Laying of a weld bead generates crevices both across the bead itself and at the bead/parent material interface which may initiate pitting earlier than if these crevices were not present. The production of heat-tinted surfaces for examination has a certain degree of randomness or unpredictability. Quantifying surface characteristics, such as the affected area by a particular degree of tinting or even a clear definition of the degree of tinting is difficult.

The stagnant conditions of the test do not exploit the deficiencies of the oxide film that may occur in the flow conditions in a piping network. Fluid friction as well as the abrasive action of any fluid borne particles could strip the oxide from the steel exposing the chromium-depleted layer to an aggressive environment. The effects of flow over the weld bead are not seen in this test.

ASTM standard G48 specifies a 72-hour test period in a fixed volume of corrosive media to specimen surface area. While the time frame provides a practical period in which to complete evaluation, assumptions can be erroneously made about the corrosion performance of a specimen. At the onset of the experiments it was expected that surfaces that had significant tinting would exhibit the most severe pitting corrosion. When the experiments were concluded, some of these areas did not corrode at all. It cannot be concluded that these specimens will not corrode if exposed for longer periods of time. Longer exposure times alone will not be sufficient to determine the pitting characteristics. The volume of corrosive media in this experiment is fixed and over time the corrodant is consumed. The time to break down the thicker oxide layer is a function of the corrodant available. It is possible the chloride ions in solution were consumed as the oxide layer was broken down but the concentration of free chlorine was reduced to level that could no longer support the corrosion process.

The number of variables associated with welding and the difficulty in quantifying them has resulted a qualitative assessment of the effects of heat tint on stainless steel welds.

9. Conclusions

Corrosion of stainless steel welds and adjacent areas is critical subject matter for those involved in application of these widely used materials.

The initial intent of this work was to identify a relationship between the degree of heat tinting and the pitting behavior. Based on the reviewed literature, the expected trend was an increase in the severity of pitting proportional to the severity of the heat tinting as identified by an increasingly darker colour. While the observed pitting behavior was more complex than the expected results, there were significant inferences;

1. As pitting corrosion occurs in two distinct phases, namely initiation and propagation, these phases are affected differently by the severity of heat tint scale.
2. Welded samples contain varying degrees of heat-tinting and zones of different severity, as identified by different colours, appear to have a galvanic influence on the pitting behavior of each other.
3. When heat tint scale is present in any degree, corrosion of the weld metal is promoted over other areas in the vicinity of the weld.

Given the number of mechanical, metallurgical and environmental factors that are detrimental to the pitting resistance of 316L stainless steel and the synergistic interaction of them, care must be taken to control as many of these variables as possible. Heat tint scale is the most variable factor in the corrosion of stainless steel welds and given that its

presence can promote the activity of other corrosion mechanisms such as MIC, it should be closely controlled and acceptance should be at a minimum.

10. References

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Appendix A Welding Procedure

WELDING PROCEDURE SPECIFICATION

[redacted] | 5312-6-1 | REVISION NO.: 1 | DATE: OCT. 1997 | SPECIFICATION: [redacted] ASME SECT. IX; ASME B31.3

Company Name/Location [redacted]
Supporting PQR No. 5[redacted]
Welding Process (es) GTAW Types MANUAL

JOINTS (QW-402)

Groove Design SINGLE VEE BUTT
Backing: Yes ____ No X
Backing Material (Type) N/A
Preparation Method SAW CUT/MACHINING/GRINDING

BASE METALS (QW-403)

BASE METALS	1	2
P. No.	8	8
Group No.	1	1
Specification No.	SA 182 / SA 312 / SA 358 / SA 403	
Grade/Type	F316L / TP316L / 316L / WP316L	
% Carbon (max.)	0.03	0.03
C.E. (max.)	N/A	N/A
Nominal Pipe Thickness	3.0	3.0
Thickness Range	2.2 - 4.5	2.2 - 4.5
Nominal Pipe Dia.	4"	4"
Pipe Diameter Range	2" - 8"	2" - 8"

Other ____

FILLER METALS (QW-404)

F No. 6 Other ____
A No. 8 Other ____
Spec. No. (SFA) SFA 5.9
AWS No. (Class) ER 316L
Brand Name LA ER316L

Size of Electrode SEE TABLE 1.0
Size of Filler SEE TABLE 1.0
Electrode-Flux (Class) N/A
Other SFA 5.12 EWTh-2 ELECTRODE

POSITION (QW-405)

Position of Groove ALL
Welding Progression UP FOR VERTICAL
Other 6G-FIXED FOR PQT

PREHEAT (QW-406)

Preheat Temp. 10 °C
Interpass Temp. 150 °C MAX.
Preheat Maintenance 10 °C MIN.
Preheat Method FLAME (TORCH)
Other ____

POSTWELD HEAT TREATMENT (QW-407)

Temperature NOT REQUIRED FOR THIS WPS
Time Range N/A
Other ____

GAS (QW-408)

Shielding Gas (es) ARGON
Percent Composition (mixtures) 100% WELDING GRADE
Flow Rate 10 - 15 L/min (21 - 32 CFH)
Gas Backing ARGON, 100% WELDING GRADE, 20 - 30 L/min (42 - 64 CFH) *
Trailing Shielding Gas Composition N/A

Other * PURGE PRIOR TO WELDING AT 23 L/min (50 CFH) FOR 2 MINUTES PER 300mm OF PIPE LENGTH

ELECTRICAL CHARACTERISTICS (QW-409)

Current DC Polarity SP
Amps SEE TABLE 1.0 Volts SEE TABLE 1.0
Other ____

CONTINUED ON PAGE 2

REV. NO.	DATE	EXPLANATION	REV. NO.	DATE	EXPLANATION
0	OCT. 7/97	FOR REVIEW PRIOR TO PQT			
1	OCT. 31/97	FOR PRODUCTION			

[redacted]

Engineer's Stamp

REGISTERED PROFESSIONAL ENGINEER [redacted] PROVINCE OF NEW[redacted]

[redacted]

WELDING PROCEDURE SPECIFICATION

No.	REVISION NO.:	DATE	SPECIFICATION:
5312-6-1	1	OCT. 1997	[redacted] ASME SECT. IX; ASME B31.3

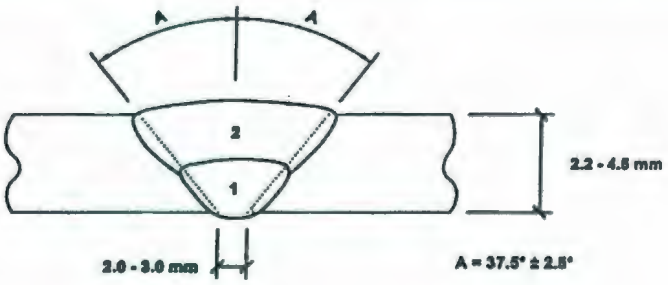
Company Name/Location [redacted]
Supporting PQR No. [redacted]
Welding Process (es) GTAW Types MANUAL

TECHNIQUE (QW-410)

String or Weave Bead STRINGER or SLIGHT WEAVE
Orifice or Gas Cup Size 10 mm
Initial & Interpass Cleaning (Brushing, Grinding, etc.)
WIRE BRUSH AND/OR LIGHT GRINDING (USE STAINLESS STEEL BRUSHES AND EQUIPMENT DEDICATED TO STAINLESS WORK)
Method of Back Gouging NONE
Oscillation N/A

TECHNIQUE (QW-410) - cont'd.

Contact Tube to Work Distance N/A
Multiple or Single Pass (per side) MULTIPLE
Multiple or Single Electrodes SINGLE
Travel Speed (Range) SEE TABLE 1.0
Other



NOTE:

1) USE 4" NPS Sch.10S (3.0 mm WT) PIPE TO PIPE FOR PQT.
2) PASS AND LAYER SEQUENCE MAY VARY SLIGHTLY FROM WELDER TO WELDER.

TYPICAL PASS AND LAYER SEQUENCE

Pass	Process	Electrode Diameter	Filler Diameter	Current	Voltage	Travel Speed (mm/min)	Heat Input (kJ/mm)
1	GTAW	2.4mm	2.4mm	65 - 75	9 - 10	49 - 58	0.60 - 0.91
2	GTAW	2.4mm	2.4mm	75 - 85	9 - 10	48 - 53	0.76 - 1.13

TABLE 1.0 - PARAMETERS

AOC/Brown & Root Canada	Engineer's Stamp
[redacted]	REGISTERED PROFESSIONAL ENGINEER PROVINCE OF NEWFOUNDLAND [redacted]

Appendix B Mill Test Report

CPI INDUSTRIES CO., LTD

MILL TEST REPORT

ISO9001:2000 CERTIFICATE (Certificate No.:1902Q13362RIM) DATE OF ISSUE:2004/12/14

CUSTOMER:. NORCA	CERTIFICATE NO. :2004-11-003-8
P.O.NO.: 25150	ORDER NO. :2004-11-003
COMMODITY: STAINLESS STEEL SEAMLESS PIPE.	GRADE :ASTM A312 -01a TP316/TP316L
CONDINTION: COLD FINISH / SOLUTION TREATED / PICKLED / PLAIN END.	HEAT NO. :F4055

CHEMICAL CONTENTS (WT%)

ELEMENTS	C	Mn	P	S	Si	Ni	Cr	Mo	
SPECIFICATION	≤0.035	≤2.00	≤0.045	≤0.030	≤1.00	10.0~14.0	16.0~18.0	2.00~3.00	
RESULTS (PRODUCT)	0.023	1.16	0.031	0.004	0.31	12.17	16.42	2.12	

PHYSICAL PROPERTIES

Dimensions			Bundle No.	Pieces	Weight (kg)	0.2%YS (Mpa) >205	T S (Mpa) >515	EL (%) >35	FLARING TEST	FLATTENING TEST	HARDNESS HRB <90	EDDY CURRENT TEST (100%)
NPS	W.T (SCH)	Length (feet)										
3/4"	10S	20	04-11-167	75	594	290	580	60.0	OK	OK	73	OK
2"	40S	20	04-11-67	100	3371	360	605	46.0	OK	OK	76	OK
1/2"	80S	20	04-10-257	100	1004	325	615	60.0	OK	OK	75	OK

REMARKS:
AS PER ASTM A312/ASME SA312-01a
WALL THICKNESS TOLERANCE AS PER ASTM A312-01a
SOLUTION HEAT TREATMENT :1050°C X 1.5m/min.
NO WELD REPAIR WAS PERFORMED
FREE FROM MERCURY CONTAMINATION
FREE OF RADIATION CONTAMINATION
MEASUREMENT & SURFACE: OK
IN COMPLIANCE TO NACE MR0175-2002
MILL TEST REPORT CONFORM TO EN 10204/3.1B

I,WE HEREBY CERTIFY THAT THE MATERIAL DESCRIBED HEREIN HAS BEEN TESTED AND THE TEST RESULTS ARE IN COMPLIANCE WITH THE TERMS OF THE PURCHASE ORDER OR CONTRACT
2.THE CERTIFICATE SHALL NOT BE REPRODUCED, EXCEPT IN FULL, WITHOUT THE WRITTEN APPROVALOF THE COMPANY.

CPI INDUSTRIES CO., LTD

MANAGER OF QUALITY ASSURANCE DEPARTMENT

Appendix C Certificate of Compliance

(Welding Filler Material)

CENTRAL WIRE
1 North St., Perth, Ontario, Canada, K7H 2X2
Certificate of Compliance / Relève de Contrôle

Customer / Client: AVESTA POLARIT STAINLESS
3178 ABBOTT ROAD
ORCHARD PARK NY
14127 USA

Customer P.O. No. / No. de Commande: B252562

Part No. / Pièce: WTW08--SP

Our Job No. / Référence: 60377

Alloy / Alliage: ER316L

Size / Diamètre: 0.09375"(3/32)

Specification: ASME SFA5.9 CERTIFIED BY CWB TO AWS A5.9

HEAT ANALYSIS / ANALYSE DE COULÉE

HEAT	C	CR	NI	MO	MN	SI	P	S	FE
469196	0.010	18.26	12.10	2.79	1.68	0.42	0.019	0.010	REM
	CU	N	TI	NB	TA	NB_TA	V	ZR	SN
	0.12	0.042	0.005	0.010			0.040		
	AL	PB	CO	CE	ZR	FERRITE/FERRITE	W	TRE	NB
	0.004		0.047			8.0			
	B	CO	O	AS					

Net Weight: 46.10 lbs

PHYSICAL PROPERTIES / PROPRIÉTÉS MÉCANIQUES

Size / Diamètre	Tensile / Résistance à la traction (KSI)	Yield (0.2%) / Limite d'Élasticité (KSI)	Elongation / Allongement (%)

Other:

We certify we have obtained the following physical properties upon testing as per specification and have released this material against the above purchase order.

Nous certifions que nous avons obtenu les résultats physiques en mettant à l'essais des échantillons pris conformément à la spécification et que nous fournissons ce matériel en conformité avec le bon de commande ci-dessus.

Q.A. _____

(Signed by...T.G.BLAIR
For Quality Assurance Manager

Tuesday, September 30, 2003

Appendix D AWS D18.2:1999 Guide to Weld Discoloration Levels on Inside of Austenitic Stainless Steel Tube

Key Words Austenitic stainless steel, tube welds, backing gas purity, heat tint, discoloration

AWS D18.2:1999
An American National Standard

Abstract

This standard addresses factors that affect weld discoloration on the inside of austenitic stainless steel tube. The document contains a color illustration relating the discoloration to the oxygen content of the backing shielding gas.

Guide to Weld Discoloration Levels on Inside of Austenitic Stainless Steel Tube

1. Scope. This standard provides a visual comparison guide that can be used to specify surface discoloration (heat-tint) criteria for sanitary (hygienic) welds in austenitic stainless steel tube.

2. The Tube Sample. The tube shown below was prepared by making 10 full-penetration autogenous welds on the outside diameter of a 2-in. (50-mm) 316L stainless steel tube. Welds on 304L tubing showed no significant difference in heat tint from 316L. The torch shielding gas was 95% argon, 5% hydrogen (with <6 parts per million [ppm] of oxygen, moisture, and hydrocarbons) to assure full-penetration welds. The hydrogen addition to the torch shielding gas is considered to have no effect on the heat-affected zone (HAZ) heat-tint oxide on the inside surface. To provide controlled amounts of oxygen in the backing gas, medical-grade compressed air was mixed with 99.996% min pure argon (<5 ppm of oxygen, moisture, and hydrocarbons). The oxygen content was measured with a calibrated commercial oxygen indicator. The amount of oxygen in the backing gas was measured to be as follows:

No. 1—10 ppm	No. 3—50 ppm	No. 5—200 ppm	No. 7—1000 ppm	No. 9—12 500 ppm
No. 2—25 ppm	No. 4—100 ppm	No. 6—500 ppm	No. 8—5000 ppm	No. 10—25 000 ppm

Weld Discoloration Levels on Inside of Austenitic Stainless Steel Tube

3. The illustration should be used as a reference to identify the degree of heat tint oxide by number, and not to specify oxygen limits in the backing gas. The acceptable degree of heat tint can vary with different service environments. The cost involved in obtaining very low levels of heat tint should be considered when specifying such levels.

The amount of heat-tint oxide and its appearance can be influenced by factors other than oxygen, such as:

- High levels of moisture in the backing gas can increase the degree of heat-tint.
- Contaminants, such as hydrocarbons, moisture, and some types of particulate on the surface prior to welding, can affect discoloration levels.
- Hydrogen in the argon backing gas can significantly reduce the amount of heat-tint oxide.
- The metal's surface finish can affect the appearance of heat tint.

American Welding Society
550 N.W. LeJeune Road, Miami, Florida 33126

Appendix E Sample Photos

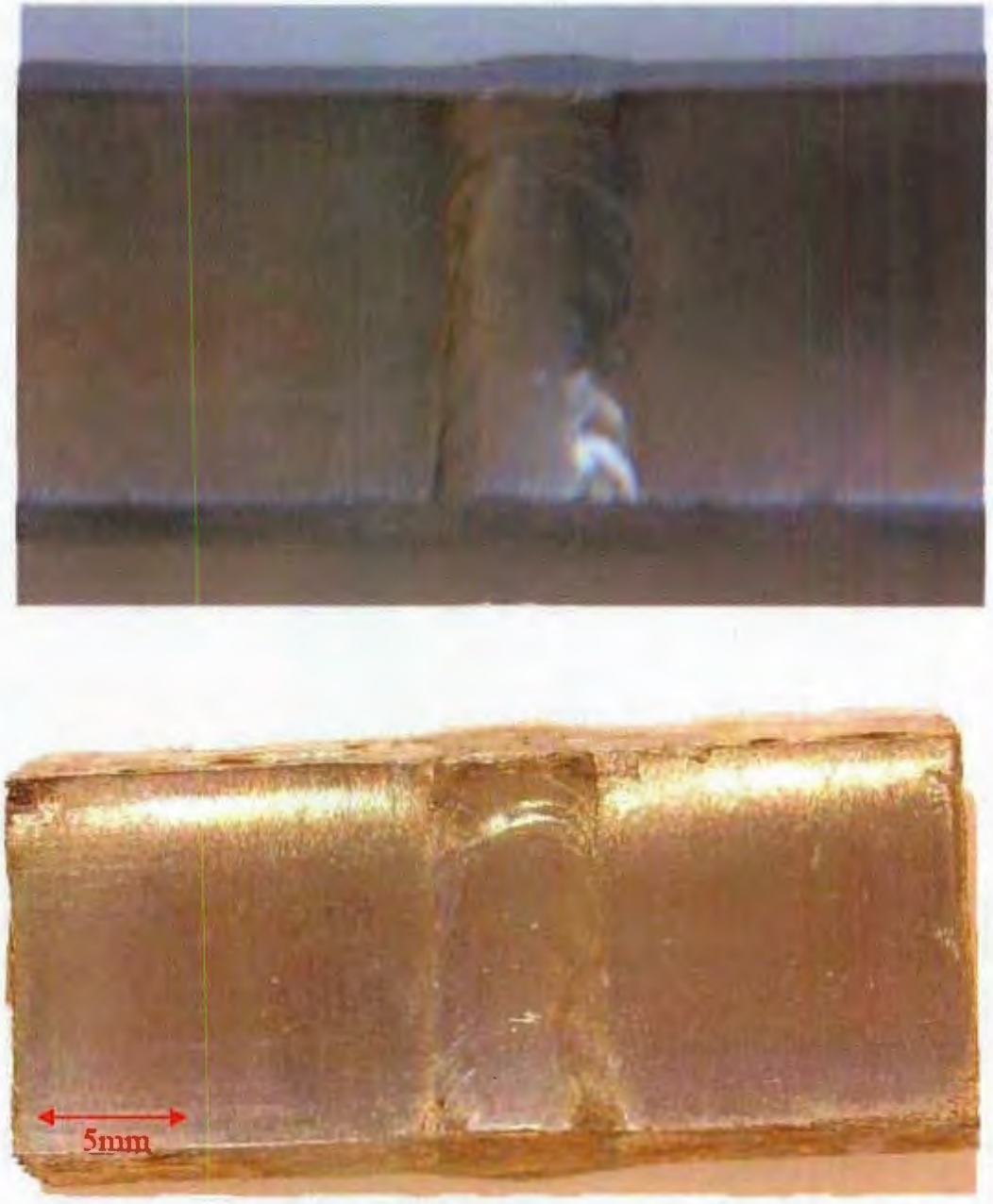
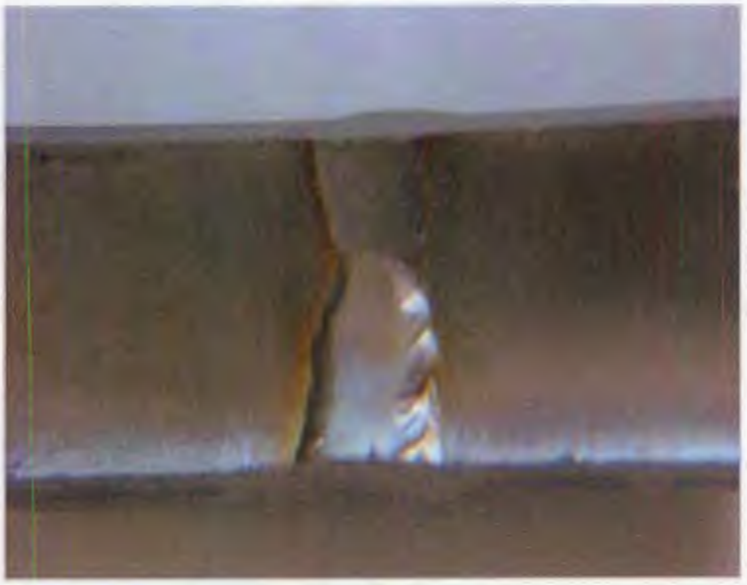


Figure 7 Sample 1-1 before (top) and after (bottom) immersion testing. No corrosion was noted after 72 hours.



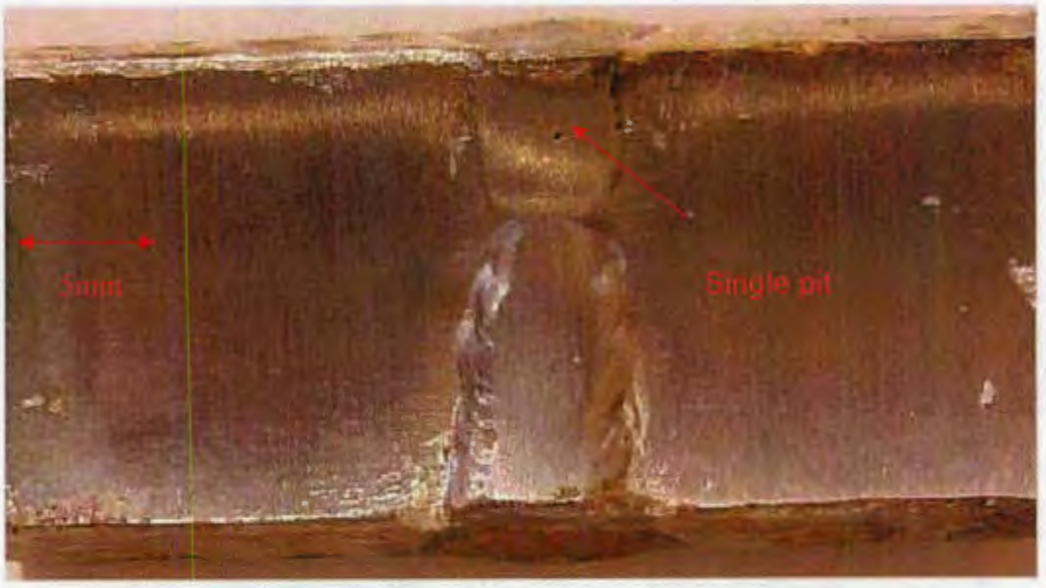


Figure 8 Sample 1-5 exhibiting single pit. Rust staining around the pit may have come from iron contamination.

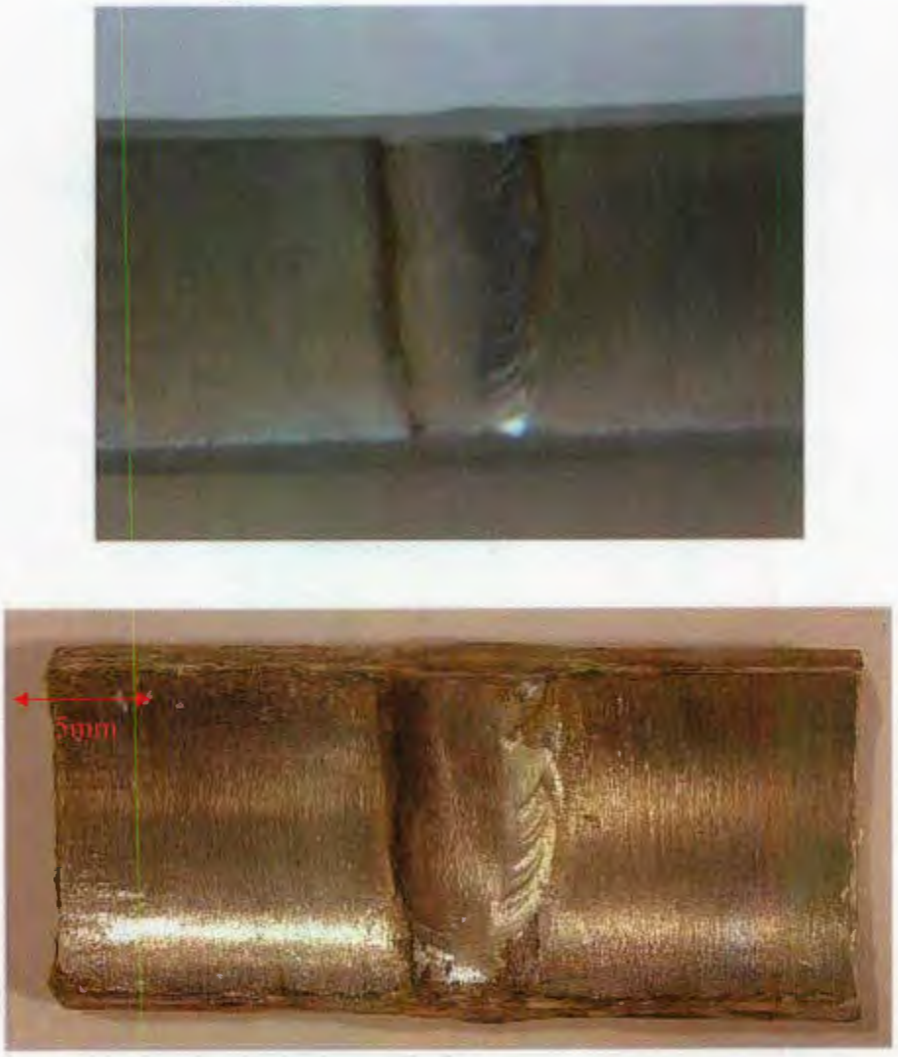


Figure 9 Sample 1-6 Epoxy leakage over the edge of the sample resulted in Under Deposit Corrosion or UDC

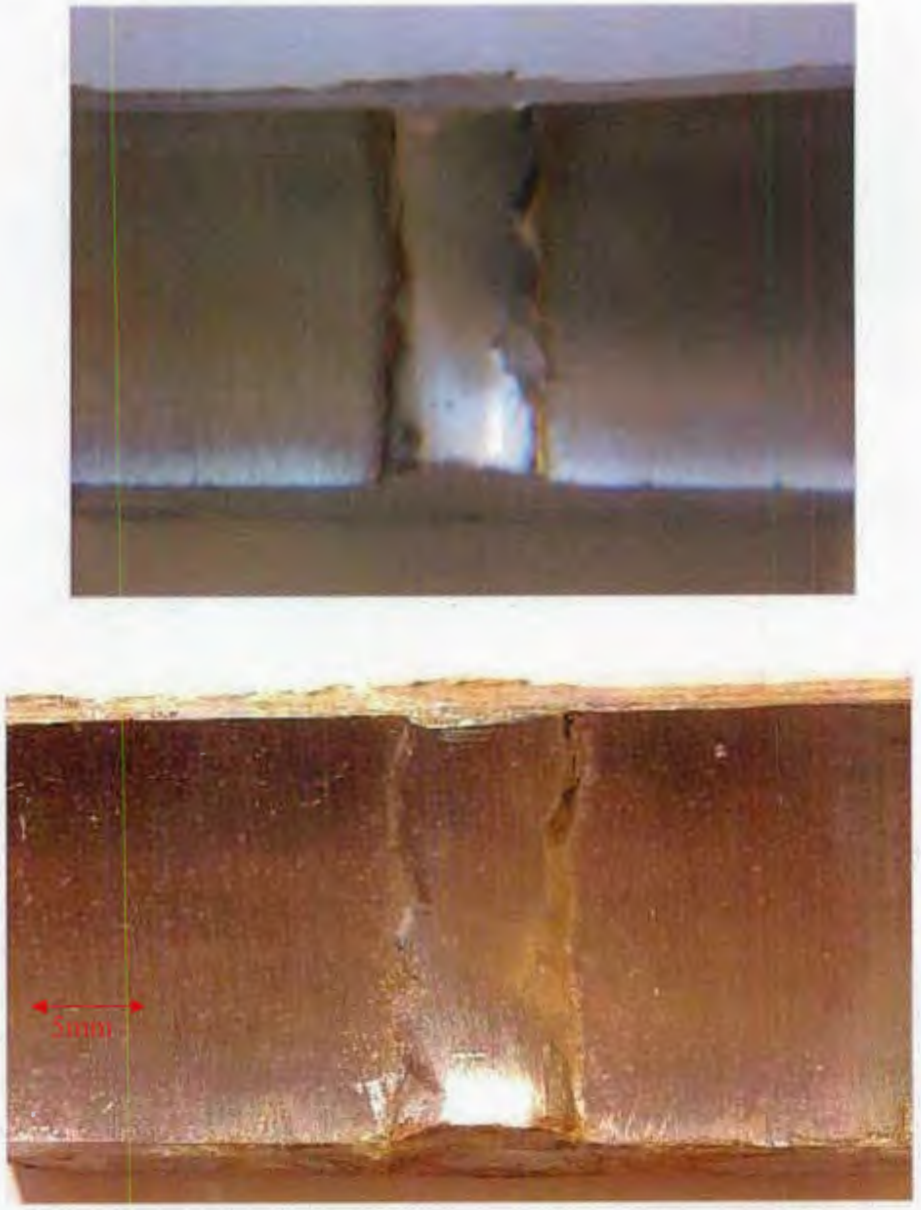


Figure 10 Sample 1-7. Free of visible corrosion after 72 hour immersion test.

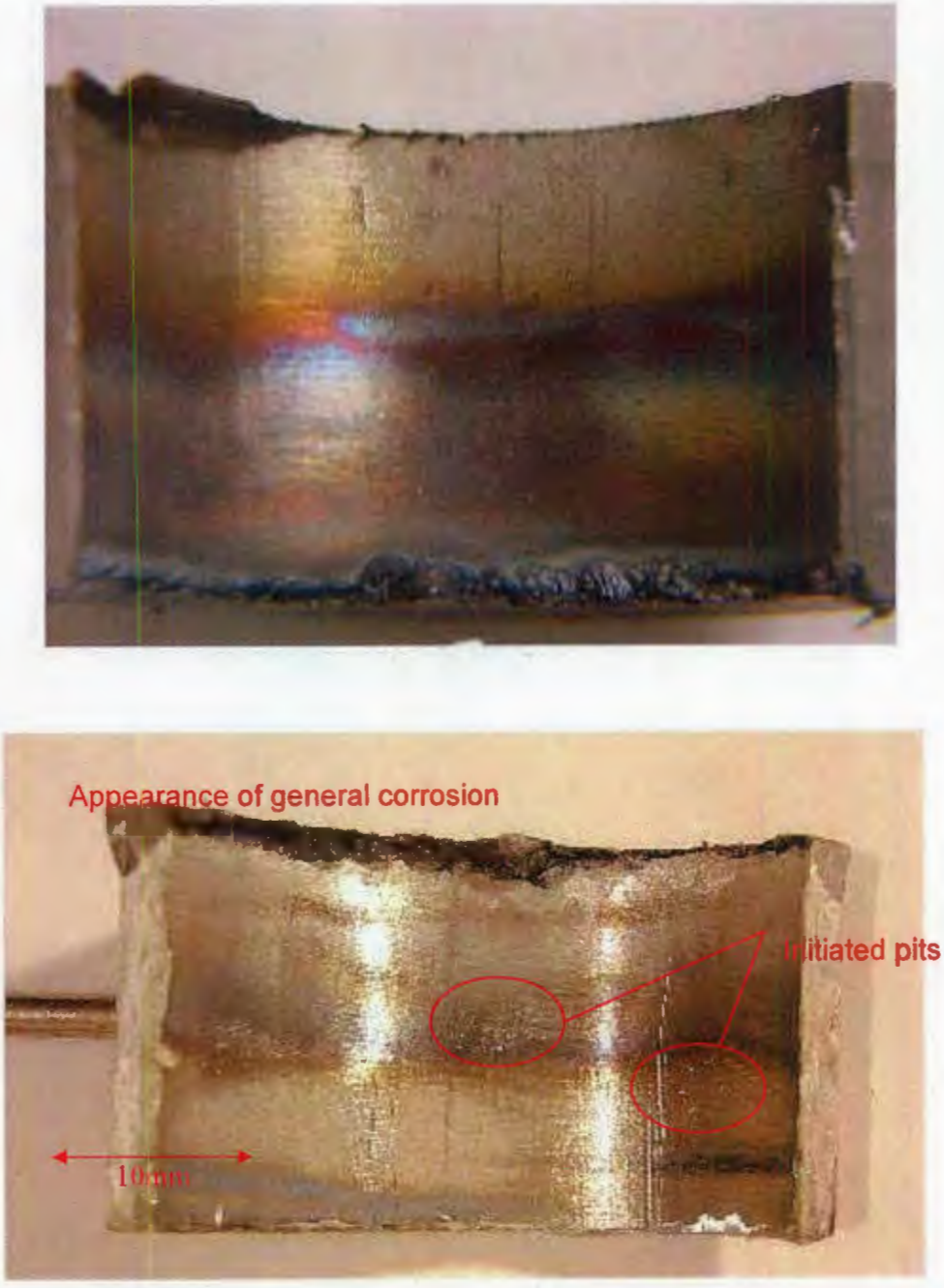


Figure 11 Sample 2-3 is nearly completely tinted.

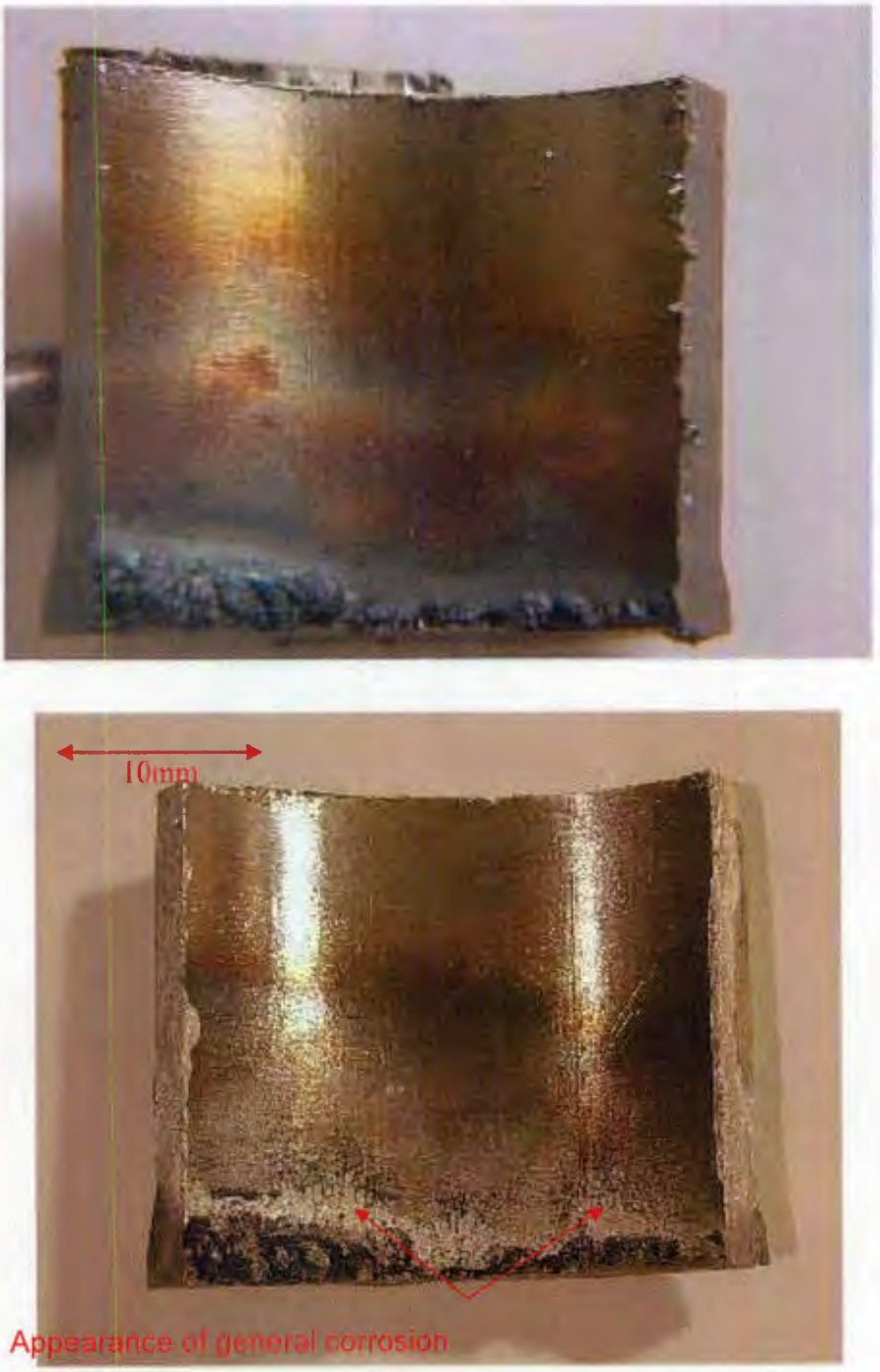


Figure 12 Sample 2-6 exhibits general corrosion in areas of heaviest tinting.

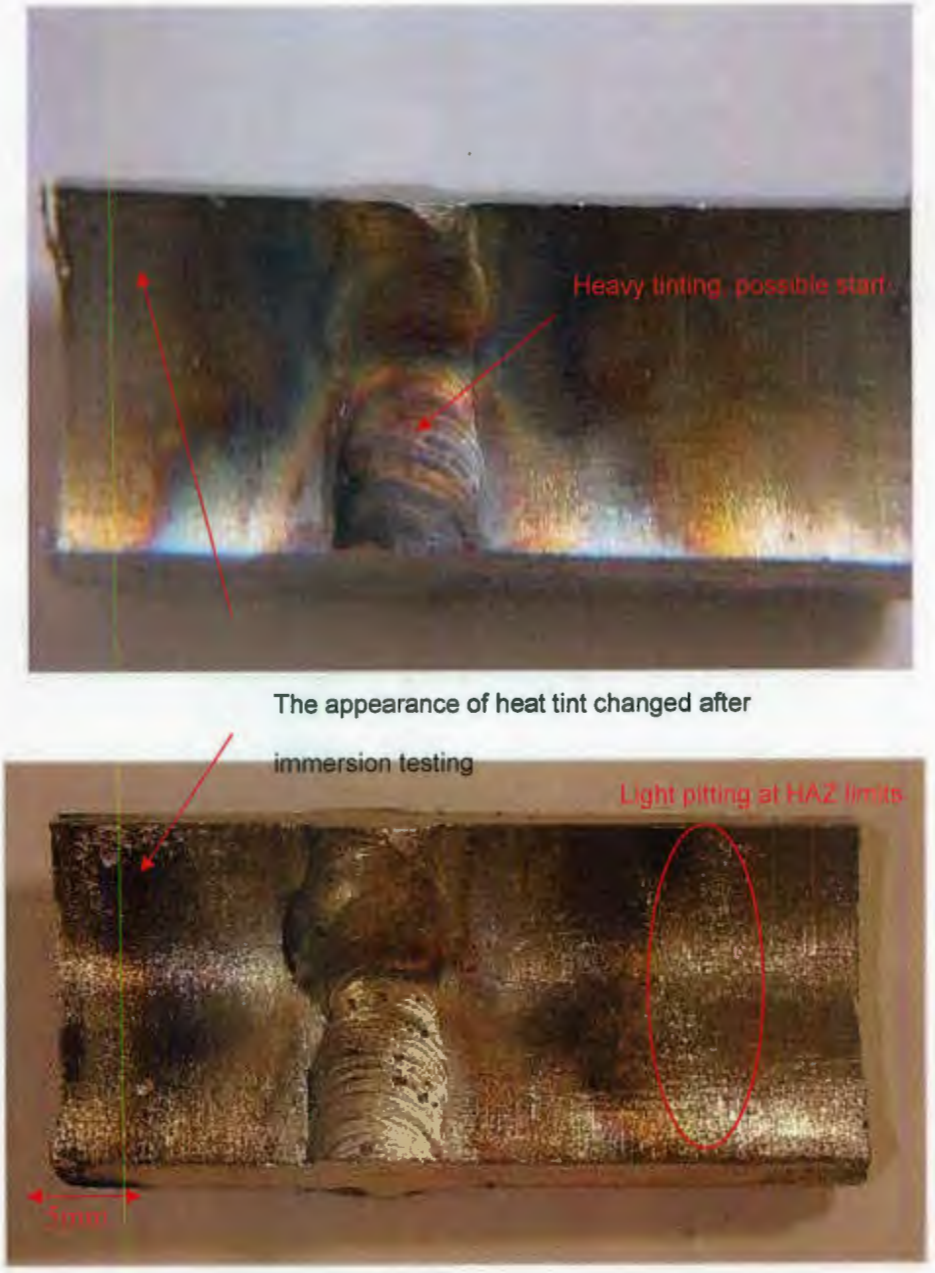


Figure 13 Sample 3-1 shows a varied pitting behavior.

Figure 14 Sample 3-5

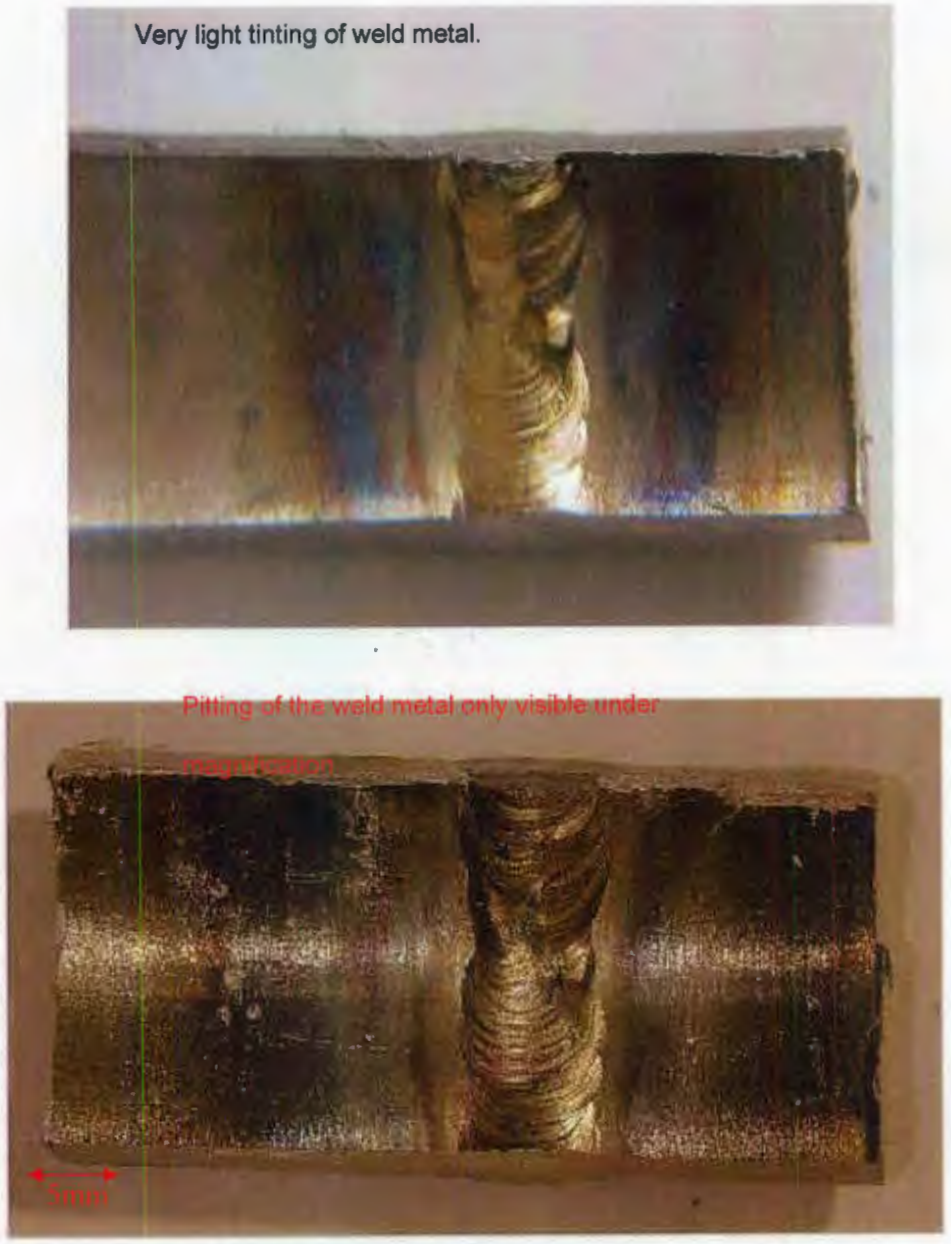


Figure 15 Sample 3-6. Similar corrosion patterns as sample 3-5, with the exception of the weld metal. Pitting in the weld bead of this sample is only visible under magnification.

Shallow dense pitting of the parent material

Figure 16 Sample 3-7. Pitting is observed in the parent material but not in the tinted area. There is a severe pit in the weld metal.

Figure 17 Sample 3-8. Pitting at the HAZ limits is so dense and shallow it has the appearance of general corrosion. Pitting follows linear striations across the HAZ. Corrosion to the right of the weld is a result of epoxy on the surface.

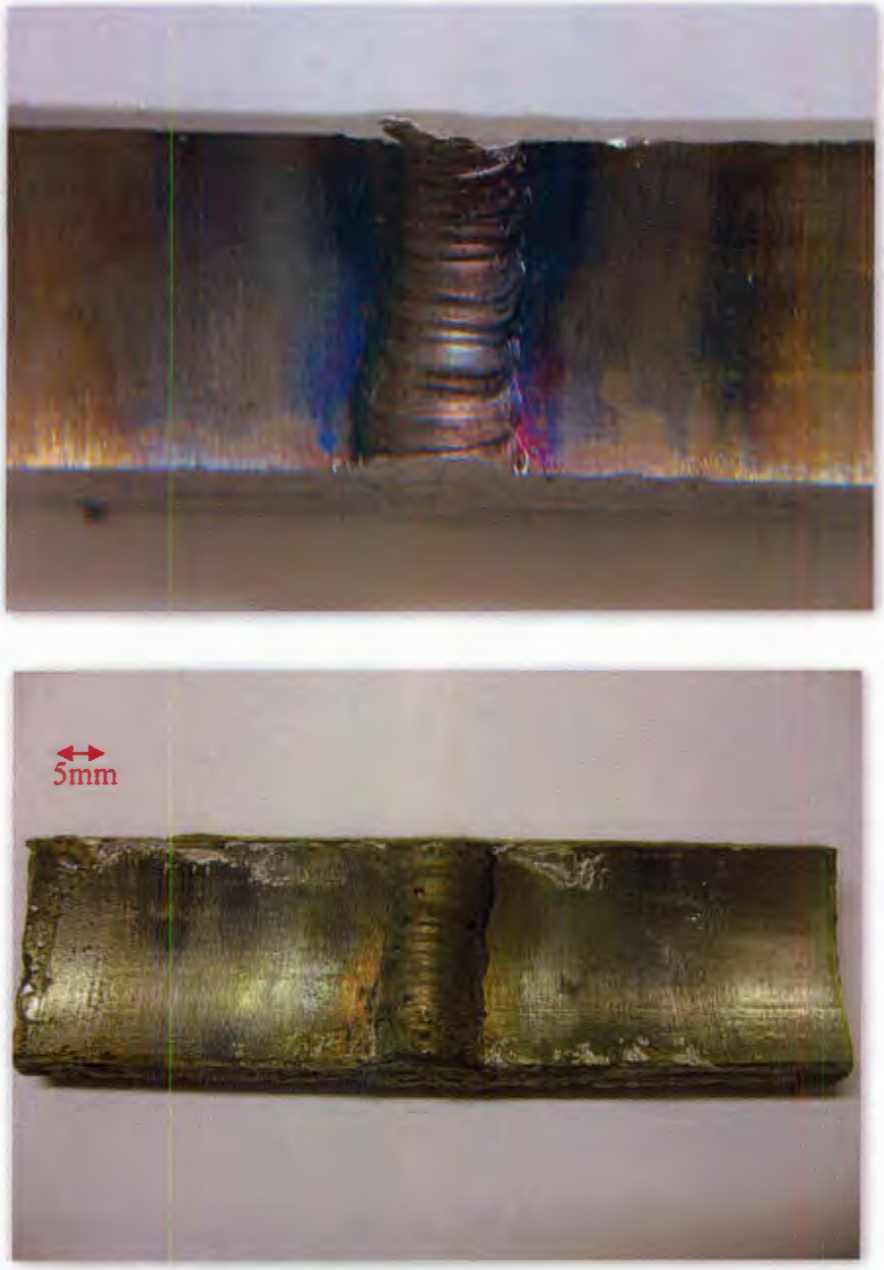


Figure 18 Sample 4-2. Pitting at the HAZ limits and defined boundaries between colours. Epoxy on the sample surface induced corrosion in those areas.

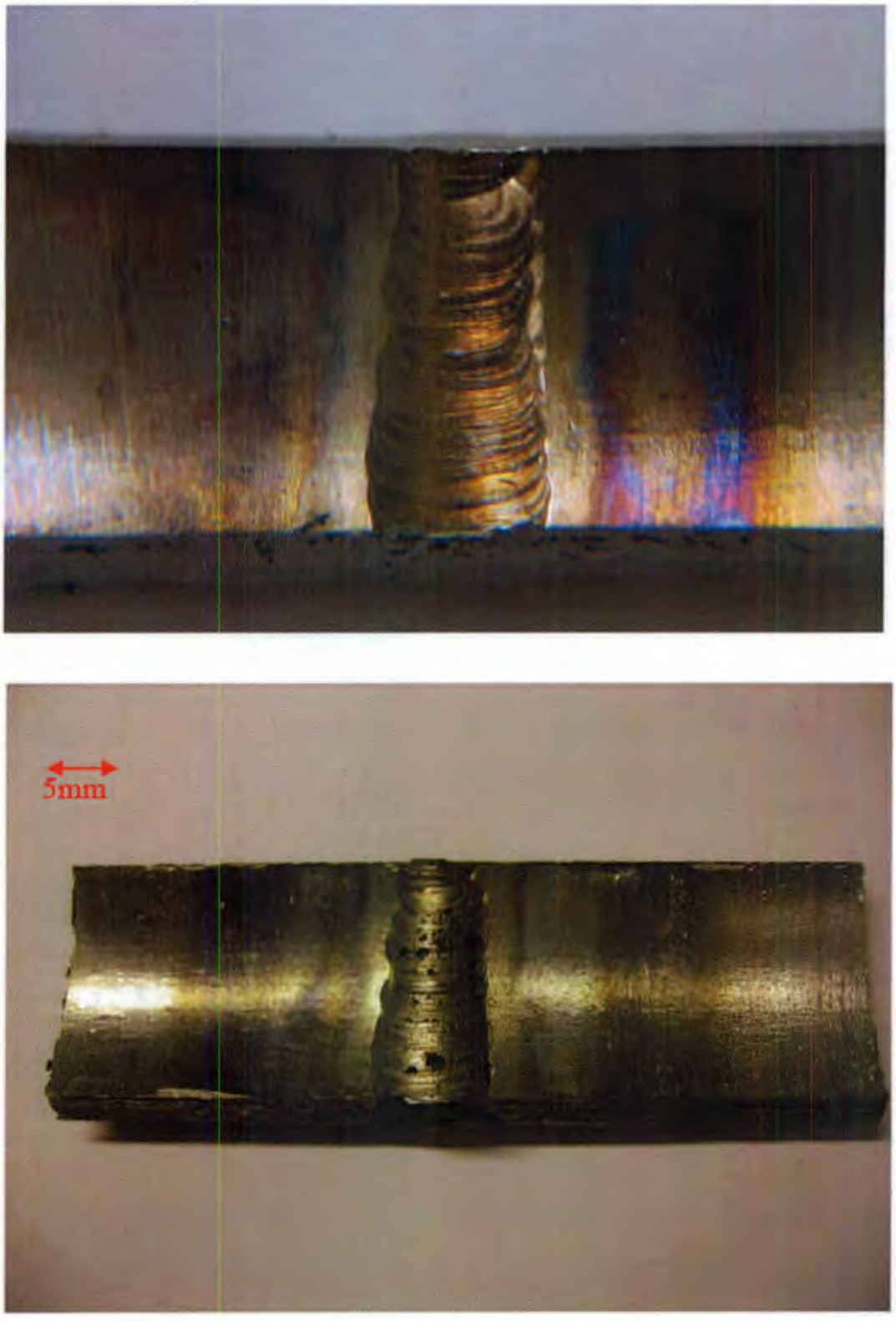


Figure 19 Sample 4-4 Pitting of the parent material and weld metal.

Figure 20 Sample 4-5. Pitting of the parent material and weld metal. Tinted areas are free of visible pits.